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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

EDWARD L. NICHOLS

ERNEST MERRITT, and FREDERICK BEDELL

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APRIL 1901

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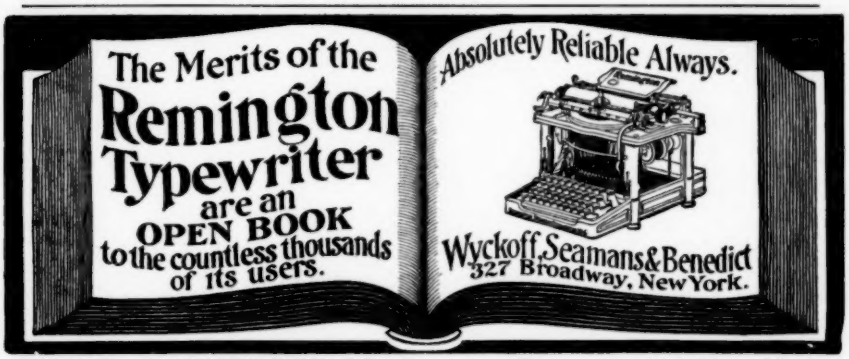

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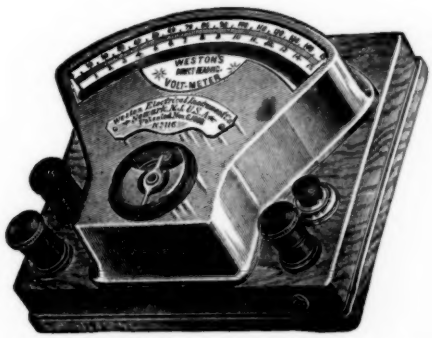

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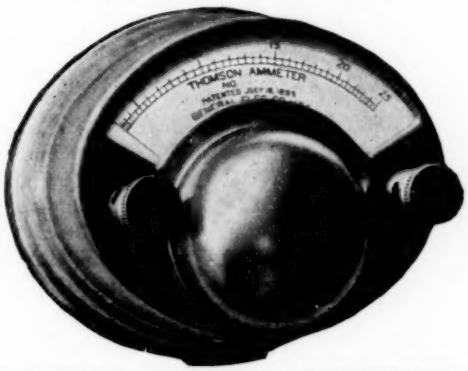

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THE

PHYSICAL REVIEW.

EXPERIMENTAL STUDIES ON THE RESONANCE OF CONICAL, TRUNCO-CONICAL AND CYLINDRICAL AIR-COLUMNS.[1]

By Victor Mahillon.

1°. All persons who have studied organography know how many prejudices are still to be encountered and how indispensable is the assistance of acoustics in shedding light on obscure points. It must be admitted that the manufacture of breath instruments, undoubtedly the most complicated of all branches of instrument making, is exactly in proportion to its importance and difficulty, the one in which this unfortunate state of affairs is most marked. False theories founded on insufficiently studied facts abound; empiricism is about the only guide.

The author has not escaped from errors caused by this situation. It costs nothing to confess this, and, furthermore, the beginnings of the catalogue are there to bear witness to this fact. But these errors could not be avoided; therefore they will be forgiven for this good reason, in the first place, and, in the second, because the evident proof of a constant search for the truth will be found alongside of each mistake.

It is not claimed, by any means, that full light has been cast on this branch of organography by thus setting forth and grouping together the results of a long series of patient trials. One thought only has prevailed through it all, that this work may be

[1] This paper is a translation by Major F. A. Mahon, U. S. Engineers, of the original account of studies carried on for nearly twenty-five years by M. Victor Mahillon while bringing together and cataloging the collection of the Museum of Instruments of the Conservatory of Music, at Brussels. [See Catalogue de la collection instrumentale du Musée du Conservatoire Royal de Musique à Bruxelles, par M. Victor Mahillon, Conservateur du Musée.]

useful, by setting forth the fruits of much toil, in saving those who come after us from falling into similar errors. It is believed also that these investigations will be useful in still another way. It is this—as they were made on all sorts of shapes of tubes and on all sorts of ways of producing vibrations, they have revealed hitherto unnoted phenomena, a knowledge of which will assist, to a certain though undoubtedly modest extent, in determining the laws which govern the vibrations of air-columns in a way more exact than that now taught by acoustics.

2°. In order to facilitate the setting forth of the subject, the principal laws, as now laid down, will be called briefly to mind. Observations on these laws will be reserved for the special cases which will arise in the course of this study.

The length of an open tube is equal to that of a single sound wave; the length of a stopped tube of the same pitch is equal to the half-length of the same wave.

The length of the single wave is the space traversed in the surrounding medium, the air, by the vibratory motion imparted to this medium by a single vibration of the vibrating body.

The velocity of 340 meters per second is that generally adopted in calculations for the propagation of the vibratory motion.

3°. The author has stated already, in his *Essay on Classification*,[1] that the opinion which he holds on the subject of sound and its formation differs not a little from that which is accepted generally. He maintains that sound is exclusively the result of the vibratory motion of the surrounding air, and that no air no sound. This importance is not given to the air as a mere vehicle; the author believes that the motion of the air is the very sound. This motion, which is silent until it strikes the auditory apparatus, only becomes really sound at the very moment of impact.

Three principal qualities are recognized in the sensations of hearing: *intensity*, arising from the force with which the vibratory motion in started; *pitch*, or degree of acuteness, which depends on the rapidity of this motion; and finally *timbre* or tone quality, which results from the more or less complex shape of the vibratory motion imparted to the air.

The tone quality of instruments is distinguished solely by the

[1] Catalogue du Musée, t. I., 2de édition, p. 1.

form of the vibratory motion given to the air, and by the relative intensity of the fundamental sound and its harmonies. There is no sound of steel, wood, strings, etc.; there are only different vibratory motions imparted to the surrounding medium, their effects being designated and distinguished by the use of terms which recall their origin.[1]

Temperature in degrees Fahrenheit.	Temperature in degrees Centigrade.	Velocity of sound in meters per second at the indicated temperature.	Number of vibrations given at the indicated temperature by a tube tuned to 870 single vibrations at the temperature of 15° Centigrade.		Length of the wave produced by a sound of 870 single vibrations at the indicated temperature.	
			Single vibrations.	Double vibrations.	Single waves open tubes.	Half single waves stopped tubes.
32.	0	332.	847.03	423.51	0m.382	0m.191
33.8	1	332.6	848.56	424.28	.382	.191
35.6	2	333.2	850.09	425.04	.383	.191
37.4	3	333.8	851.62	425.81	.384	.192
39.2	4	334.4	853.15	426.57	.384	.192
41.	5	335.	854.68	427.34	.385	.192
42.8	6	335.6	856.21	428.10	.386	.193
44.6	7	336.2	857.74	428.87	.386	.193
46.4	8	336.8	859.27	429.63	.387	.193
48.2	9	337.4	860.80	430.40	.388	.194
50.	10	338.	862.33	431.16	.389	.194
51.8	11	338.6	863.86	431.93	.389	.194
53.6	12	339.2	865.39	432.69	.390	.195
55.4	13	339.8	866.93	433.46	.390	.195
57.2	14	340.4	868.46	434.23	.391	.195
59.	**15**	**341.**	**870.**	**435.**	**.392**	**.196**
60.8	16	341.6	871.53	435.76	.393	.196
62.6	17	342.2	873.06	436.53	.394	.197
64.4	18	342.8	974.59	437.29	.394	.197
66.2	19	343.4	876.12	438.06	.395	.197
68.0	20	344.0	877.65	438.82	.395	.197
69.8	21	344.6	879.18	439.59	.396	.198
71.6	22	345.2	880.71	440.35	.397	.198
73.4	23	345.8	882.24	441.12	.397	.198
75.2	24	346.4	883.77	441.88	.398	.199
77.	25	347.	885.30	442.65	.399	.199
78.8	26	347.6	886.83	443.41	.400	.200
80.6	27	348.2	888.36	444.18	.400	.200
82.4	28	348.8	889.90	444.95	.400	.200
84.2	29	349.4	891.43	445.71	.401	.200
86.	30	350.	892.96	446.48	.402	.201

[1] Let it be borne in mind that if the walls which confine the air-column and give it its shape be sufficiently smooth and stiff, the material of which they are made has no effect on the shape of the vibration and, consequently, it has no influence on the quality of the sound.

The velocity of sound, continuing to use the consecrated term, increases with the rise of the temperature of the air; hence this rise should be considered in calculating the length of waves and tubes.

The table on previous page gives the effect of temperature on a tube tuned to A, the 58th degree of the scale of sounds.[1]

It is seen by this table that the influence of temperature has a value which may not be neglected. The velocity of propagation varies by about 60 centimeters per second,[2] and the rate of vibration of the A of 870 single vibrations per second also varies by 1.5308 single vibrations for each centigrade degree of temperature. It follows from this that an open tube giving this A would be 382 millimeters long at the temperature of melting ice (0° Centigrade, or 32° Fahrenheit), whereas at 30° C. (86° F.) the same A would require a tube 402 millimeters in length. The intonations of these two tubes, compared at the same temperature, would vary by a full semi-tone.[3]

[1] The *C*, the first degree of the lowest octave, the one known in organ-building as the 32-foot octave, is taken as the starting point. From this is obtained the following scale with all its intermediate degrees:

1st octave,	*C* 1st degree,	6th octave,	*C* 61st degree.
2d "	*C* 13th "	7th "	*C* 73d "
3d "	*C* 25th "	8th "	*C* 85th "
4th "	*C* 37th "	9th "	*C* 97th "
5th "	*C* 49th "	10th "	*C* 109th "

By means of this method, approved and recommended by the international jury of the Universal Exposition at Brussels in 1897 (G. Serpette, Rapport sur les opérations du jury), the position of a sound is determined more than easily by the use of indices which have no base and which vary from one country to another.

[2] John Tyndall, On Sound, p. 26.

[3] This effect of raised pitch is still more marked for wind instruments whose air-column is set in vibration by the breath. The effect of the latter, of which the mean temperature is 32° C., or 89.6° F. (according to Gréhant, cited by Kuss and Duval—Traité de Psysiologie, p. 434—the temperature of the breath is 35.5 at 22° and 29.7 at 6°), is, in our climates, where the surrounding temperature is generally below this figure, to warm the air-columns, to increase the rate of vibration, and, consequently, to cause the pitch to rise very sensibly; the colder the air the more marked is this effect. These facts have an important bearing on the tuning of wind instruments. The mean temperature of concert halls, especially in winter, being about 20° C. (68° F.), *all* instruments without exception should be tuned at this temperature. A unison would be obtained in this way between those which are less sensitive to temperature, piano and harmonium, for example, and those more sensitive to this influence, such as the organ and all wind or breath instruments. Before the latter are regulated they should have been played for some minutes.

4°. Assuming the velocity of the propagation of sound generally adopted for acoustic calculations, viz: 340 meters (1,115 feet) per second, this number must be divided by the number of single vibrations per second if the length of the sound wave be desired, this length being the space traversed by the vibratory motion of the air during a single vibration of the vibrating body. Thus the length of the single wave corresponding to the A, 58th degree of the scale of sounds, is obtained thus:

$$\frac{340 \text{ meters}}{870 \text{ single vibrations}} = 0.39 \text{ meter.}$$

5°. Theoretically, therefore, an open tube 0.390 m. long should give the A of 870 single vibrations, and this same sound should be produced equally well by a stopped tube

$$\frac{0.390}{2} = 0.195 \text{ m. long.}$$

6°. Practice shows that these data are inaccurate, or at least incomplete. If the air be made to vibrate in the two cases, by blowing into these tubes in such a way as to set their air-columns in motion in the simplest way, that is, by blowing across the open orifices of the tubes held firmly against the lower lip, sounds will be obtained sensibly lower than the A of 870 single vibrations, and it has been noticed further that the stopped tube gives a slightly lower sound than the open tube.

7°. To what cause must this difference between the teaching of theory and that of practice be assigned? To this circumstance, it is believed; that the influence of the tube is felt beyond its bound-

In like manner the air sent into the pipes of an organ by the bellows should be brought first to a temperature of 20° C.

The French commission of 1859, when it fixed the pitch of the A_3 (58th degree of the scale of sounds) at 870 single vibrations with a temperature of 15° C. (59° F.), wished only to state absolutely the conditions under which the vibrations of the standard had been attained. The idea that it wished to set at 15° C. the temperature at which instruments should be regulated according to its *tonarium*, cannot be attributed to it. Furthermore, it would be impossible to maintain this temperature, whereas 20° is the temperature of our halls, as a general rule, at all seasons of the year. It is known that the influence of temperature on steel tuning forks is so small that it can be regarded as nothing in practice. This circumstance should cause them to be preferred to any other apparatus intended to give the pitch.

aries, thus causing a wave longer than the theoretical wave and, consequently, a sound lower than the one expected.

8°. This difference was something interesting to examine closely, and led naturally to studying it in its results on the different shapes of tubes used in the construction of wind or breath instruments. These shapes appear under three main categories: *open tubes; partly stopped tubes; stopped tubes.*

9°. But while belonging to one of these three categories, tubes may differ very sensibly in their details. All the special shapes met in the course of these studies have been summed up by the making of eleven tubes. These tubes, shown in outline in Fig. 1, vary between 0.290 m. (11.42 inches) and 0.240 m. (9.45 inches) in length; the figures at the end show the diameters in millimeters at those points, and the accompanying letters will be used hereafter to designate them.

I. OPEN TUBES.

10°. The tubes thus named are entirely open at both ends. Hence their air-columns are in communication with the surrounding air at each extremity; whence follows the existence at each end of a loop of vibration for all the sounds of its harmonic resonance. The loop of vibration is that part of the wave where the air has a maximum motion of vibration without any change in pressure or density. At the node of vibration, on the contrary, the air undergoes continual changes of density and pressure while the velocity of the vibratory motion at test point is zero. The fundamental sound and the harmonics of open tubes are to each other as the natural series of whole numbers 1, 2, 3, 4, etc. The fundamental sound of a tube is the lowest sound which it can give. It is the one corresponding to the calculated length of the tube. It is produced by the least pressure exerted on the air-column to excite its vibratory motion.

Experience shows that it is very difficult to cause columns of air, set in motion by blowing across one of the orifices of the tube, to produce sounds of a certain intensity. Still the motion of the air-column resulting from this form of winding is sufficient to determine very accurately the height of the sound, and, with a little practice, a certain intensity is imparted to it. With perhaps one excep-

tion, the *Nay*, the flute of Musulman countries, this style of tube has not been used in the manufacture of instruments. The *Nay* itself is not a wholly open tube at its upper end, because, in order to

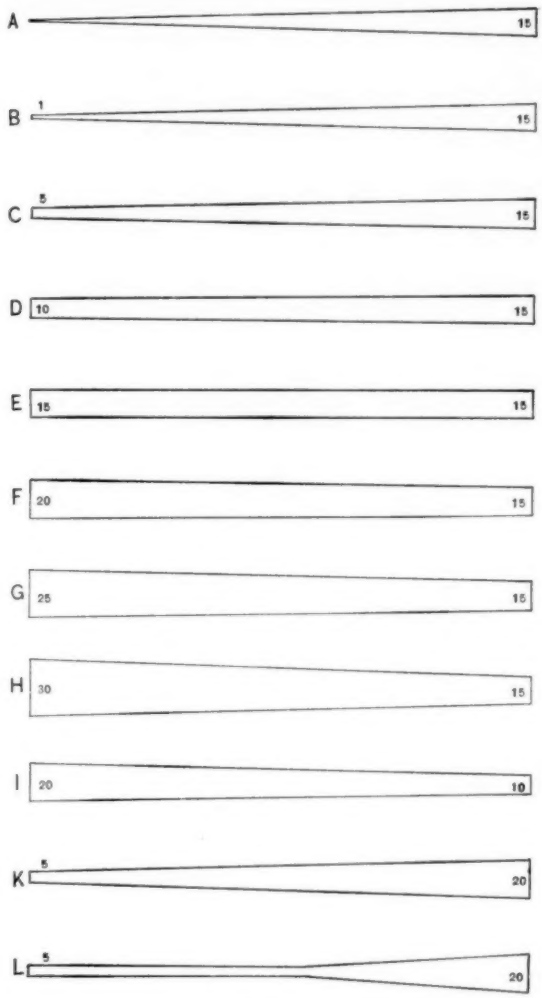


Fig. 1.

facilitate setting the column of air in vibration, the performer partly covers the opening of the tubes with his lips (see § 15).

11°. It has been stated (§ 6) that, when experimenting with a tube of exactly the length of the sound wave, a deeper sound than that

indicated by theory is obtained. Numerous trials show that the difference between the data of theory and those of practice increase with the diameter of the tube. If the sounds of two cylindrical tubes of the same length but of different diameters be compared, the sound of the tube having the smaller diameter will be sensibly higher than that of the other. The observation of this fact gave the direction in which to seek the following formula of correction, noted already in 1874.[1]

The length of a cylindrical tube open at both ends is, for a given sound, equal to the length of the single wave of this sound less a length equal to ¾ of the diameter of the tube. It has been seen (§ 4) that the length of the single wave of a sound of 870 single vibrations per second is 390 mm. If a tube 20 mm. in diameter be required to produce this sound its length will be:

$$390 - 20 \times \tfrac{3}{4} = 375 \text{ mm.}$$

In fact, an open tube of this length set in vibration in this way, gives exactly the normal A of 870 single vibrations at the temperature of 14° C. (57.2° F.).

Another and equally important result follows from this fact, viz: that theory lacks in accuracy when it teaches that, to cause one tube to give a sound an octavo lower than the sound of another tube, the length of the first tube should be double that of the second. *It is the theoretical length of the wave which must be doubled,* and this doubled length must be lessened by ¾ the diameter of the tube. Thus, to obtain an A of 435 single vibrations from a tube 20 mm. in diameter, the theoretical length of the wave corresponding to the A of 870 single vibrations is doubled, and from that is taken three-fourths of the diameter of the tube:

$$390 \times 2 - 20 \times \tfrac{3}{4} = 780 - 20 \times \tfrac{3}{4} = 765 \text{ mm.}$$

A tube of these dimensions will give very accurately the A of 435 single vibrations at the temperature of 14° C.

12°. The following results are obtained from general observations on the eleven before-mentioned tubes:

(*a*) The pitch of the sound produced by blowing across the end

[1] Eléments d'acoustiquemusicale, by V. Mahillon.

of the tube is the same whether the breath be applied at the large or the small end.

(*b*) The length of each of the eleven tubes tried is that of the single wave less three-fourths of the mean diameter.

(*c*) The harmonics obtained are proportioned to the fundamental sound of the tube. This sound is very exactly the F of 1,381 single vibrations (66th degree of the scale of sound corresponding to the normal pitch). The wave of this sound is, as shown in § 4, equal to $\frac{340}{1381} = 246$ mm. as shown in the following table :

Real length of the tube.	Length of ¼ of diameter.	Length of the single wave.
A 0m.2404	0m.0056	
B .240	.006	
C .2385	.0075	
D .2366	.0094	
E .23475	.01125	
F .2329	.0131	0m.246
G .231	.015	
H .2291	.0169	
I .23475	.01125	
K .2366	.0094	
L .2366	.0094	

As will be seen further on, an exception is made for the tube *L*, which is irregular in shape, the cylindrical tube being prolonged by one of trunco-conical form.

13°. When each of these tubes is examined by itself from the standpoint of facility in starting the vibrations of the inclosed air-columns it is noticed :

1. blowing across the small end :

(*a*) That *A*, *B*, *C*, *K*, *L* do not speak. *A* is wholly closed at the apex of the cone ; it will be considered further on. The opening at the narrow end of *B*, *C*, *K*, *L* is too small to allow the vibration of the air-column to be excited.

(*b*) That *D*, *E*, *F*, *I* speak easily, and, in addition to the fundamental sound, allow the octave, or sound 2, to be given.

(*c*) That *G*, *H* give the fundamental sound easily, and the octave with greater difficulty.

2. blowing across the large end :

(*a*) That *A*, although wholly closed at the vertex of the cone, acts as an open tube, that is, contrary to theory, its length for a given sound is equal to the single wave of that sound and, in spite of its being wholly closed, it gives the series 1, 2, 3, etc., of the harmonic scale and not the odd-numbered ones alone.

(This peculiarity of conical tubes closed at the vertex was discovered first, it is believed, by the celebrated English physicist Wheatstone about 1832. It has been mentioned already in D. J. Blaikley's very remarkable study, *Acoustics in Relation to Wind Instruments*. This very important fact will be taken up again further on.)

(*b*) That *B*, *C*, *D*, *E*, *F*, *I*, *K* speak well and give easily the harmonics 2 and 3, in addition to the fundamental sound.

(*c*) That the sonorous starting (*ébraulement sonore*) of *G*, *H*, is difficult on account of their great diameter, which interferes with the production of the oscillatory motion necessary for this starting.

As these eleven tubes give the same sound F, 66th degree of the scale of sounds, it may be concluded from the preceding experiments that the effect of the bore on tubes set in vibration in the same way is almost nothing so far as the pitch of the fundamental sound is concerned, or at least that it exerts no greater influence than that mentioned in § 11. It may be well to remark that for tubes of the same length harmonics are produced rather more readily by tubes of the smaller diameter.

It has been said (§ 12) that *L* is a tube of irregular shape. If the vibratory motion be given at the large end, the fundamental sound rises a fourth, while the harmonics remain those of the tone F, common to all the other tubes. It has been observed, by experiments on other tubes, that the pitch of the fundamental sound rises as the broken lines which form the sides of the tube approach the axis more nearly, or, in other words, as the tube becomes narrower. This peculiarity of this kind of tube is not of great importance, as tubes wholly open at both ends are rarely used in manufacturing ; it does permit to be noted however that the irregular shape of the tube *L*, for the mode of applying the breath under consideration, gives a harmonic resonance which is false when compared with that of the regularly shaped tubes: cylindrical, conical and truncoconical.

II. Partly Stopped Tubes.

14°. The material impossibility of producing in tubes of large sectional area, either by the breath or even by mechanical means, the pulsations necessary to set the air-column in vibration, has caused the manufacturing industry to seek some arrangement which would permit the required action to be produced on thin sheets of air or on reduced sections. Hence, the different shapes of the mouth opening devised from time immemorial among all nations, and still utilized to-day in making all the varieties of flutes used in the organ as well as in our orchestras. Among the latter the most familiar varieties are the *flute à bec*[1] and the *traverse flute*. In both types the tube was partly closed so as to allow a thin sheet of air to be directed against the sharp angle formed on one of the sides of the tube, an arrangement which gave extreme facility in the production of the vibratory motion.

15°. The practical demonstration of this facility of sonorous emission is easy: let the tube *E*, for example, be taken. If it be held vertically against the lower lip, so as to direct the breath over the whole section of the tube, a certain amount of practice will be necessary in order to obtain a sound. But let the tube be raised so as to give it an inclination of about 45° ; then let the breath be directed against the edge opposite to that touched by the lip, care being taken to cover nearly half the orifice of the tube. The latter will speak with very great facility, and will give out a full, pure sound. The construction of the Arabian *nay*, the mode of setting which in motion has been so little understood by some historians, is based on the observance of this principle.[2]

[1] It seems easy to-day to establish the parentage of the flute à bec. The primitive type appears to have been the Arab *nay*, which was completely open at its ends; then the *siaku-hachi*, a Japanese flute, in which the end of the tube is bevelled on a part of the circumference to facilitate setting the air-column in vibration. The next step seems to have been the Chinese *lu*, of which the orifice is entirely open, but on the circumference of which was cut a small rectangular notch, the breath being directed against its edge; this same notch is found again in the flute Krena, from Bolivia; finally the Chinese *ty*, also with the rectangular notch, but closed at the orifice by the tube, thus forming a true bevelled mouth. (See Nos. 136, 714, 859, 862 and 711 of the *Catalogue du Musée.*)

[2] In describing the *lus*, or Chinese pitch pipes, Nos. 859, 860, 861 of the Catalogue du Musée, mention was made of the theory set forth in 1596 by the Chinese Prince, Tsai-Gu, on the subject of the relation to be maintained between the length and the

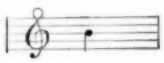
16°. The partial closing of the tube, by causing an inevitable slackening in the velocity of vibration, brings about a lowering of the pitch. And all our flutes give lower sounds than those indicated by theory, even when the lowering due to the diameter has been considered. It cannot be otherwise; all flutes are partly closed at the mouth hole, and the smaller the opening used for exciting the vibratory motion the greater the lowering of the pitch. The evidence seems to be that the partial closing demands a tube of a certain diameter, while, on the other hand, narrow tubes must be used to facilitate the production of the harmonics. The oldest makers of the flute *à bec* overcame the difficulty happily by using a trunco-conical bore; they had thus at their disposal the wide part at which to place the mouth, and in order to assure facility of emission, a relatively narrow air-column, or at least one much more narrow than a cylindrical air-column would have given. This is not the case with a *traverse* flute; the side mouth by which the air-column is set in vibration does not require a wide opening, therefore the old *traverse* flutes were cylindrical as they are to-day. It was only in the seventeenth century that instrument makers, imitating the flute *à bec*, adopted the trunco-conical shape of the air-column, placing the mouth hole at the largest part of the tube.

17°. A question arises here, Is it possible to calculate the lowering which this partial closing causes in the pitch of the tube?

It is very difficult. But, what numerous trials have given the means of noting, is this: *the influence of this closing is inversely proportional to the length of the tube*, and this is a fact of a certain weight. Beyond this the result obtained must be determined experimentally.

diameter of the pipe. According to this theory, in which the author, by reason of his studies, could not help being interested, the lengths and diameters increased in a constant ratio. The analysis of this theory showed that the length increased for each of the twelve descending semi-tones of the octave in the ratio of $1 : \sqrt[12]{2} = 1 : 1.0594631$, whereas the diameter increased in the ratio of $1 : \sqrt[24]{2} = 1 : 1.0292857$. This theory gives, unfortunately, only approximate results, and, again, the length of the first pipe, the starting point for calculating the others, must be found empirically. What led the writer first into error as to the true value of this theory, which is very interesting for its origin and the time at which it was propounded, was that at that time he was wholly ignorant of the influence of the partial closing of the tubes caused by the way in which the air-columns of these *lus* are set in vibration, and that, undoubtedly, an imperfect test had accounted for the defect noted to-day.

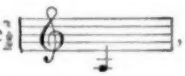
In order to make this clearer the following empirical method was established; it will supply what is lacking in the above explanation.

For example: let there be a tube which when fully open gives the sound at the normal pitch. This sound produced by 976.5 single vibrations in a second, has a wave-length of

$$\frac{340}{976.5} = 348 \text{ mm.}$$

The tube being 19 mm. in diameter, three quarters of this diameter is 14.25 mm. This then is the amount by which the length of the wave must be reduced in order to have the length of the tube, hence

$$\begin{array}{rr} & 348 \\ \text{less} & 14.25 \\ \hline & 333.75 \text{ mm.} = \text{the length desired.} \end{array}$$

But it is found experimentally that, by the partial closing of the tube resulting from the adoption of any kind of mouthpiece, the intonation falls a full tone. This lowering can be determined in wave-length as follows:

390 mm., length of single wave of A
less 348 mm. " " " B
difference 42 mm., or the value of lowering caused by the partial closing of the tube which sounds the B, 60th degree of the scale of sounds. If it were desired to calculate the length to be given to a tube of the same diameter intended to give the , 46th degree of the same scale, the following method is used:

The length of the wave of B is.....	348 mm.
The lowering caused by the partial closing is.....	42 "
Length of the A next below is.....	390 mm.
Double this length to bring it to the next octave below.	780 mm.

But, as has been said at the beginning of this paragraph, the influence of the partial closing is inversely proportioned to the length; hence, for a length double

390 mm., the effect will be one-half less and there must be taken from the total length..... 21 mm.

759 mm.

and, to withdraw also the influence of the diameter of the tube, $19 \times \frac{3}{4} =$..... 14 mm.

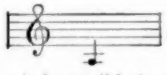
length of the tube sought for the .... 745 mm.

which is confirmed by experience.

The complication of the phenomenon is great, and, it will be understood, its influence on the theoretical teaching of flute construction is enormous. It will be confessed that in spite of this importance the matter was neglected entirely in the author's *Elements d' acoustique !*[1]

18°. In trying the first ten tubes[2] as mentioned in §13 and in closing them to the same extent, deeper sounds are obtained by this partial covering than those of the *entirely* open tubes. But it is of the utmost importance to remark that, under these conditions, the intonations are alike from whatever side the air-column is set in vibration, that is to say whether it be at the larger or the smaller end. It is also to be remarked that in these air-columns, which are set in vibration by an opening in the direction of the axis, the lowering of the fundamental sound occurs also in the harmonics, so that their vibratory relation remains true ; that is, it continues to be that of the open tubes, that of the natural series of whole numbers 1, 2, 3, 4, etc.

19°. The phenomenon of the harmonic resonance of the traverse flute is not exactly the same. The air-column of this last instrument is set in vibration through an opening made in the wall of the tube and smaller in diameter than the diameter of the air-column.

[1] This complication is increased further by the influence of the holes made in the sides of the bore. Thus the tube which gives the , the length of which has just been found to be 745 mm. will have its pitch sensibly lowered so soon as the lateral holes required for forming its scale have been bored. This influence is explained in this way : each of the openings made in the more or less thick walls of the tube adds somewhat to the length of the air-column which it contains.

[2] The reason why the tube *L* is excepted has been given.

The result of this peculiar position is that the lowering caused by the partial closing of the tube is greater in the fundamental sound than in its harmonics. The cavity which lies between the plug which closes the upper end of the tube and the opening through which the air-column is set in vibration is intended to correct this difference.[1] This cavity has no influence on the height of the fundamental sound; hence certain players who use the adjusting screw, which controls the movement of the plug, to tune the flute, do so wrongly. But if this cavity has no effect on the fundamental sound, it acts on the harmonics whose relation with the fundamental it corrects by lowering them.

As the air-column remains in communication at both ends with the surrounding air, it will be well to recall what was said in § 10: that a loop of vibration exists at each end of these open or partly closed tubes, no matter which of the sounds produced by the harmonic resonance may be uttered.

III. Closed or Stopped Tubes.

20°. By this term are known all those tubes which are closed at one end and are open at the other. In scientific terms they are: all those tubes which have a node of vibration at one end and a loop of vibration at the other. The vibratory motion in them is propagated from the outer to the inner end, from the bell to the mouthpiece, and not in the reverse direction as is generally believed and as is the case for open or partly stopped tubes. All the reed and all the mouthpiece instruments will be borne hereafter in this category.

The air-column contained in these tubes can be set in vibration in three different ways:

A by the breath directed against the edge of the open end, the other end being stopped.

B by a mouthpiece.

C by a reed.

Returning to the tubes, each of the ways of producing vibrations will be examined, noting that, whichever be the means used in the

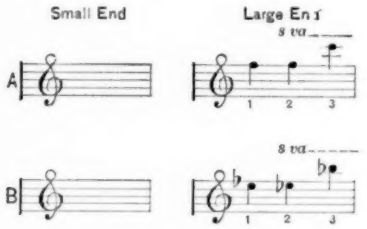
[1] This difference is proportional to the difference between the diameter of the air-column and that of the side hole which acts as a mouth; thus it is greater in the flute than in the piccolo.

case of stopped tubes, the law of vibration does not change and that any change in the length of the tubes would cause no further modification in them.

A. VIBRATION BY THE BREATH.

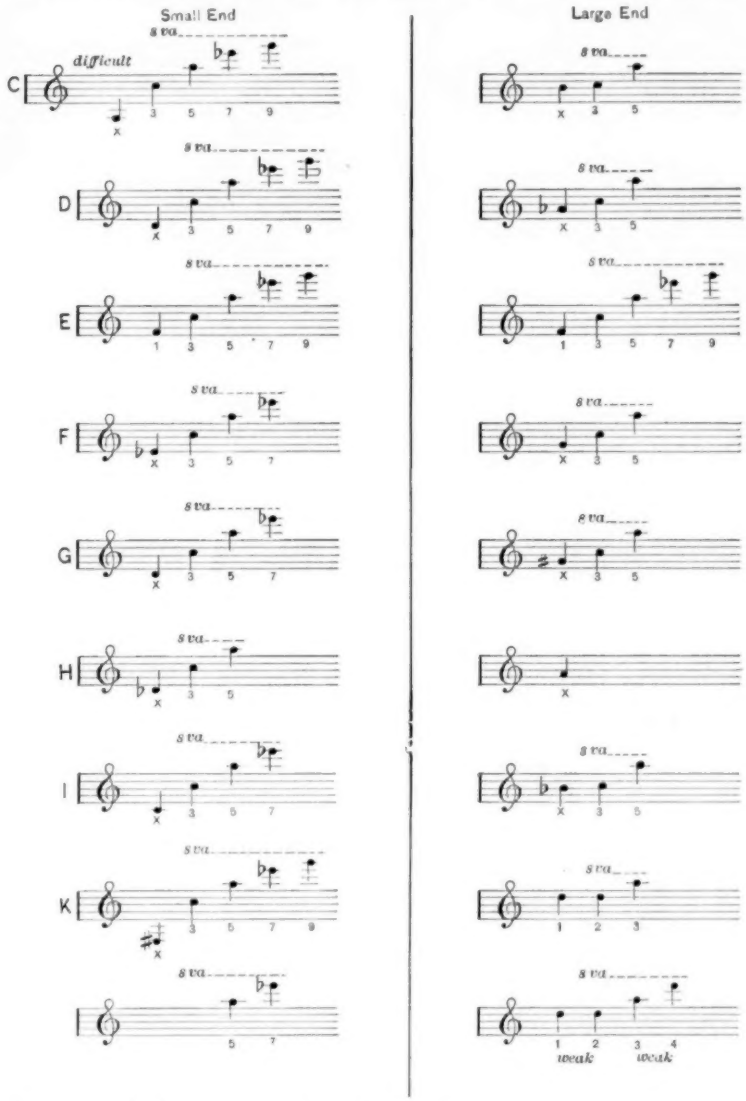
21°. This way of setting the air-chamber in vibration has been applied only in the *syringa*, commonly called the *pipes of Pan.* This instrument is made generally of cylindrical tubes of reed, stopped at one end, and set together side by side. According to the present theory, the length of each of these tubes is equal to that of half a single wave. Experience has shown that a correction is equally needed here. In fact it has been found that, to calculate the length of a cylindrical tube stopped at one end and intended to give a certain predetermined sound, *the length of the single wave of this sound must be reduced by a length equal to one-half the diameter of the tube.*[1] It is deemed useless to dwell longer on this mode of correction. What was said in connection with open tubes will suffice to show exactly the practical way of applying it.

22°. In the following table have been placed side by side the harmonic resonances obtained from each one of the eleven tubes by blowing alternately into the large and small ends, *the opposite end being stopped by the flat of the hand:*



[1] It may be interesting to know that the maximum length of the tubes of which the fundamental sound can be produced by this way of blowing is very nearly the length of the 44th degree of the scale of sounds. The diameter has a certain influence on the production of the fundamental sound. If the diameter were very narrow, the tube would give harmonic 3 instead of the fundamental sound. It has been found experimentally that for a tube, vibrating under good conditions, to produce its fundamental sound, the diameter must be $\frac{1}{20}$ of its length.

23°. Trying each of the tubes separately it is found:

(*a*) That A and B cannot be made to vibrate by the small end, as A has no opening and that of B is too small. Set in vibration from

the large end these same air-columns have a harmonic resonance exactly like that of the open tubes, *in spite of the fact that they are stopped.* This fact is in opposition to the existing theory as to the laws of vibration of air-columns.

(*b*) That E, the cylindrical tube, is the only one whose air-column vibrates in conformity with the laws of existing theory. The length of this tube giving the fundamental sound F, 54th degree of the scale of sounds, is equal to that of a single half-wave corrected as indicated in § 21, and its harmonics follow the series of odd numbers, 1, 3, 5, 7, etc.

(*c*) That the tube *H*, when the breath is applied at the large end gives only the fundamental sound, and that with a certain difficulty, on account of the exaggerated size of this diameter.

(*d*) That the tubes *C*, *D*, *F*, *G* (and this is a point of prime importance as it leads to the determination of the conditions needed by a stopped tube to acquire the harmonic resonance of an open tube) continue to preserve *approximately*[1] the odd-numbered harmonics of the cylindrical tube, no matter from which end they are set in vibration, while the fundamental sound rises or falls appreciably according as the breath is applied at the large or the small end. This deviation from the fundamental sound F of the cylindrical tube is due to a slackening or a hastening of the vibratory motion; it can be stated in terms of an equal number of vibrations which generates, therefore, in the same tube, a larger interval downward than it does upward. Furthermore the intonation of the sounds marked × is only approximate.

(*e*) That when the breath is applied to the large end of the tubes *C*, *I*, they have a resonance which approaches that of the open tubes.

(*f*) That, the tube *K* possessing the harmonic resonance of an open tube, it may be concluded that, for a tube of trunco-conical form to sound the octave, *the diameter of the open end must be at least four times that of the stopped end.*

To sum up what precedes: the conical tube closed at the vertex resounds like an open tube of the same length, and its resonance causes the harmonics to be heard successively in the natural order of the numbers 1, 2, 3, 4, etc. Within limits, the trunco-conical tube acts like the conical tube, but its pitch, compared with that of the open tube, becomes lower in proportion to the diameter of the

[1] The harmonics rise or fall with the fundamental sound; it is stated that they stand *approximately* in unison with the odd-numbered harmonics of the cylindrical tube, because the variations in these sounds are much less marked than that noted in the fundamentals (see § 28, *b*).

truncated part, where the tube is stopped. An examination of the table, § 22, shows that this lowering is a minor third when compared with the intonation of the *wholly open* tube. It is needless to say that this lowering, which is a tone and a half for this small length, becomes less when a larger tube is used.

The question, why a conical tube closed at the vertex of the cone resounds like an open tube, deserves careful consideration. One would be led to believe, at first glance, in the influence of the mass of air contained in the tube. This is not so. It is known that the volume of air contained in a cylindrical tube is four times as great as that contained in a conical tube of the same length and having the same diameter at the base.

Furthermore, if the mass of the air entered the question, the influence of the diameter would be much greater than that stated in §§ 11 and 12. The fact that the pitch of the cylindrical tube drops a full octave by the closing of one of its ends (§ 22) leaves it to be supposed that the phenomenon of the conical or trunco-conical tube, of given proportions, resounding like an open tube, is due to the reflexion of the vibratory motion, and that it is more rapid against the oblique sides of these trunco-conical tubes than against the bottom or stopper of the cylindrical tubes.

B. Vibration by Means of a Mouthpiece.

24°. If the ends of any one of the tubes be struck against the flat of the hand, the resulting fundamental sound, although very feeble, is sufficiently perceptible to allow noting that its pitch is the same as that of the sound obtained from the same tube when it is set in vibration by the breath *applied at the other end.* All the fundamental sounds of the table, § 22, are thus obtained, excepting naturally from these experiments the tubes *A* and *B*, the structure of which does not permit this form of vibration. It is well to note, however, that, as the pressure on the air-column thus obtained can only be uniform, it goes without saying that only one sound, the fundamental, can be obtained.

Hence, the excitation of the vibratory motion by striking the hand against one of the open ends of the tube is equivalent to closing this end completely, and this action does close the tube absolutely.

25°. If this means of setting the air-column in vibration be replaced by the one which consists in resting the same orifice against the lips, there is obtained a sound the same as the one given by the tube when the vibratory motion is obtained by the breath applied to the opposite end, and it is in this way that the air column of all the instruments used in the orchestra are set in vibration : cornets, bugles, horns, trombones, basses, etc. The harmonic resonances noted in the table, §22, remain absolutely the same, observing however that the division of the air-column which can be realized by the breath is not obtainable by the lips, because the latter cannot vibrate fast enough to secure movements synchronous with those which would follow from the division of the air-column caused by the production of harmonics in such short tubes. On the other hand, the air directed against one of the orifices of the tube has not sufficient energy to impart the vibratory motion to air-columns of too great length. (See note to §21.)

An inspection of the above-mentioned table shows that the only tubes suitable for the construction of our mouthpiece instruments are those of the types *B*, *K*, *L*. But, without hurting their lips, players could not set an air-column in vibration by applying the lips directly to the tube which contains it. This is why an intermediate apparatus, called a *mouthpiece*, is used ; it is, in a word, only a prolongation of the tube ending in a cup around which is worked a comparatively wide flange against which the performer places his lips. The shape of the cup has necessarily a certain influence on the tone color, and on the facility with which the air-column is set in vibration. The mouthpiece must be arranged conveniently and according to rules taught by practice or experience.

A node of vibration, with continual changes of density and pressure is found at the mouthpiece of all mouthpiece instruments ; a loop of vibration, with maximum velocities of motion is found at the bell. To blow into instruments is an improper expression ; players only blow into certain reed instruments and even then the term is rigorously exact for the cremonas only (Nos. 610 *et seq.* of the catalogue) or for instruments with an air reservoir. The air is a motive force used to put the air-column in motion, either directly (as in the flutes), or through the medium of the lips (mouthpiece instru-

ments), or through the medium of the apparatus called *reed* (clarinettes, oboes, bassoons, etc.).

26°. Hence, all the mouthpiece instruments are tubes stopped at the mouthpiece end. They possess, by reason of suitably established proportions of their air-columns, the complete harmonic resonance of the tubes *B*, *K*, *L*.

27°. Experience shows that tubes of trunco-conical form are not the ones most to be recommended for mouthpiece instruments. The tone-quality resulting from the vibration of this form of air-column is harsh and wild; it is the characteristic tone-quality of primitive instruments, made of horns of animals, and even also that of periods when the maker's art had already made some advance, as the Danish *Lur* of bronze. (See No. 1,156 of the Museum of the Conservatory.)

The progressive enlargement of the air-column must be made along certain curves, sought even in these later days by trial, which are associated in certain cases with a longer or shorter cylindrical tube.

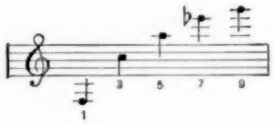
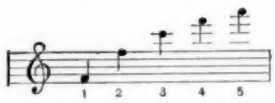
Thanks to this association being allowable, the shape of the air-column of mouthpiece instruments can be varied infinitely, and thus all the varieties of tone quality indispensable for the orchestra can be had, while the resonant qualities of trunco-conical tubes relatively to the just ratio of the harmonics with the fundamental sound are preserved.

28°. Numerous trials allow the establishment of the following facts, which do not differ from those already noted in §22 and 23:

(*a*) If a mouthpiece be applied to a cylindrical tube, the air-column vibrates like a stopped tube and only the odd-numbered harmonics are heard; furthermore the sound lacks fulness.

(*b*) So soon as the lower part of the tube is expanded and receives a conical form, the resonance improves, the fundamental sound rises as do also the harmonics, the latter approaching gradually, as the cone advances, the ratio given by the series of figures 1, 2, 3, 4, etc. This phenomenon is noticed even when the tube is enlarged for only a small part of its length at the end opposite the mouthpiece. It appears first in the upper harmonics, and reaches its

finality when the enlargement of the tube is obtained under the proportions given in the following paragraph. The annexed table will make the matter clearer. It shows the harmonic resonance of any two tubes of the same length, in F, the one cylindrical, resounding like a stopped tube, the other conical, resounding like an open tube.[1]

Cylindrical tube,

Conical tube,

The proper enlargement being applied to a cylindrical tube causes sound 1 to rise to its octave which then becomes sound 1 of the conical tube; sound 3 becomes sound 2; sound 5 becomes sound 3; sound 7 becomes sound 4; sound 9 becomes sound 5, and so on. It can be conceived that the slightest expansion given to the tube may produce the small approach required for the high sounds, but that a much more marked enlargement is needed to make the low sounds rise by the desired amount. The intervals become more and more contracted as the enlargement of the lower end of the tube progresses, and when this reaches the proportion given in the next paragraph, the twelfth 1 : 3 becomes the octave 1 : 2; the major sixth 3 : 5 becomes the fifth 2 : 3; the minor fifth 5 : 7 becomes the fourth 3 : 4; the large major third 7 : 9 becomes the major third 4 : 5, etc. It will be noticed that the difference in the intervals given by the succession of the harmonics *in the two kinds of tubes* becomes smaller and smaller, and continuing onward they might even become confounded within a very small difference. This phenomenon brings us very close to the law which governs the vibration of these air-columns. If this law cannot yet be stated in precise terms, the

[1] This scale of a cylindrical tube of which the air-column is set in vibration by a mouthpiece is only hypothetical. A cylindrical tube of sufficiently small diameter to be set in vibration by the lips, and, on the other hand, sufficiently long to give theoretically this low F, would only speak very imperfectly in practice; the low sounds would not be produced.

observed phenomena are sufficiently clear to show even now the reason why a tube may be cylindrical for a part of its length, starting from the mouthpiece, and then must become wider as the opposite end, generally called the bell, is neared.

(*c*) That the high harmonics may be in exact relation to each other without their being so to the fundamental sound (trumpet, trombone). Experience has shown that it is indispensable, in order to have the relation of an octave between the fundamental sound and sound 2, that the gradual enlargement of the air-column begin, at the least, at the middle of its length, and that the minimum ratio of the diameters of the ends of the tube be as 1 to 4. The sudden expansion called the *bell* is not included in the determination of the ratio between the extreme diameters.[1] This enlargement is a mere question of shape, of style. It is very differently made in different countries, and in some, Germany for example, it is omitted altogether, without the manufacture of the mouthpiece instruments being in any way inferior on this account.

Trumpets and trombones, as already said, do not give the fundamental sound, or at least they give it with difficulty, and its relation is not true; it is generally too low as compared with sound 2 at which the scale of these instruments begins. This defect is owing to the lower part of their air-column which only begins to expand at the last third of its length. They might be called *incomplete instruments*.

(*d*) That the brilliant tone quality (trumpet and trombone) is favored by the use of narrow tubes and that, on the other hand, the smooth unctuous tone quality characteristic of the basses is due solely to the broadness of their air-column. In these instruments,

[1] It appears from experiments made by M. Mahillon since his pamphlet was published, that the size of the bell has some influence on the sound quality. This influence is especially marked in the case of the horn of which the bell is very largely developed, and of which the peculiar, *sui generis*, sound quality may be mainly attributed to this part of the instrument. M. Mahillon noticed that as the bell was more and more cut off the soft sound quality of the horn became lost and approached the brilliant sound quality characteristic of the trombone and the trumpet.

By reason of the sharp enlargement of its bell the pitch of the horn does not change sensibly in spite of this shortening of the air-column and the high harmonics are obtained more easily. This last phenomenon is explained, in M. Mahillon's opinion, by the reduced friction of the air against the wall of the tube.

which will be called *complete*,[2] the expansion of the tube begins immediately back of the mouthpiece; in some of them the ratio between the two extreme diameters is at times 1 to 20.

29°. Variety of tone qualities follows from the many proportions which can be given to the air-column. In certain cases, it was seen in the trumpet and trombone, technical reasons make it necessary to utilize the cylindrical tube prolonged by another tube of which the diameter becomes gradually larger. But it is wrong to qualify as "conical" this shape which is given to the lower part of the air-column. The cone joined to the cylinder would not form a regular air-column, the division of the latter into aliquot parts, absolutely necessary for the production of harmonics, would be impossible and consequently the harmonics would be false with each other and with the fundamental sound. Hence the prime necessity that the tube should expand smoothly instead of being formed with walls of broken lines. This *sine qua non* condition is reached by using, as already said in §27, curved lines which continue the cylindrical part uninterruptedly, thus forming tubes of which the forms are those of surfaces of revolution generated by these curves when made to revolve about the axes of the tubes. The determination of these curves, their equations and their forms lie beyond the scope of this paper. They will form the object of a special article. Moreover, the subject is interesting only to instrument makers.

C. VIBRATION BY MEANS OF A REED.

30°. The resonance of tubes set in motion by this medium is the same as that obtained by producing the vibration with a mouthpiece. The tube, instead of being closed at its upper end by a mouthpiece, is now closed by a reed, and it is at the end of the latter that the node of vibration is found, the loop of vibration being at the

[2] The distinction between these two kinds of instruments is made in Germany. Zamminer (*die Musik und die musikalischen Instrumenten*, Giessen, 1855) calls them *Halbinstrumenten* and *Ganzinstrumenten*. There is in the orchestra but one complete mouthpiece instrument, that is, one whose scale begins with sound 1. It is the tuba or bass in B♭; it is so made because it replaced the ophiclied whose scale utilized the first octave. It will be added that this exception is not to be recommended, seeing that the present methods of instrument-making are wholly unequal to intercalating perfectly accurately the eleven chromatic degrees in the octave between sound 1 and sound 2.

other end, the bell. The reed may be single or double, it matters little which, the result is the same if the lowering of the air-column caused by the reed be the same. (See further on, §32.)

The resonant types of the oboes, English horns, bassoons, double bassoons, saxophones, are the trunco-conical tubes *B*, *K*. The cylindrical tube *E* is the type of the clarinet.

31°. This phenomenon explains the doubling of the fundamental sounds at the octave or at the twelfth above by the mere increase of pressure on the reed. From it flows evidently the necessity that all instruments with side holes—the successive opening of which has for its object the production of consecutive degrees of the scale—should preserve very exactly, from the first lateral hole next the reed, either the cone with the ratio of the diameter 1 : 4 for tubes intended to sound the octave above the fundamental, or the cylinder for those intended to sound the twelfth.

The question is often asked, why, if the shape of the reed being single or double is without influence, the double reed is used generally with trunco-conical tubes, and the single reed with cylindrical tubes? A moment's reflection gives the answer to the question. The single reed is always cut out from a tube having itself a certain diameter; the necessity of giving to the tube, at the position of the side hole nearest the reed, a diameter four times that of the tube in which the tongue of the reed is taken, evidently makes it obligatory to give the air-column a very marked conical shape, which can only be accomplished by the machinery which modern instrument-making has at its disposal. The saxophone is an example. Hence, this reed was suited exclusively to cylindrical tubes.

On the other hand, the slips of the double reed are attached very easily to a little conical tube of which the upper end has a very small section. The difficulty of giving the air-column of this tube the proportion 1 : 4 desired was not great for the means which the old makers had at their disposal. Hence, the double reed found its place necessarily when associated with the conical tube. Only exceptionally was it associated with cylindrical tubes (cremonas, cervelas).

32°. The reed not only closes the tube but, by the resistance it offers to the breath, it lowers, in proportion to its elasticity, the pitch

of the air-column.[1] It acts, furthermore, like the partial closing mentioned in § 17. What completes the comparison is that its influence is also: *inversely proportional to the length of the air-column with which it is associated.*[2]

The slips of reed used in making the reeds of breath instruments are extremely sensitive to the pressure of the breath; very great differences of pitch can be obtained by varying the pressure. The flexibility of these reeds is so great that they can set in vibration air-columns of very different lengths. It is this property of the slips of reed which allows the numerous shortenings of the air-columns by the side holes.

Metallic reeds do not possess this property. Their invariable degree of elasticity causes them to give a single sound, and when they are associated with tubes, they demand the use of air-columns in harmony with them within very narrow limits. It is enough to break the proportion to prevent the vibratory motion of the reed (Chinese *cheng*, No. 137; Siamese *khën* No. 138 of the catalogue), or, at the least to disturb its regularity, and to give rise to intonations which are painful to the ear.[3]

33°. This peculiarity of the reed to have, as it were, an intonation

[1] The lowering influence of the reed on an air-column can be shown easily. Let a clarinet mouthpiece and its reed be taken; the pitch obtained by the use of the reed will be about a tone lower than that which would be obtained by directing the breath against the lower opening opposite to the position of the reed. The pressure on the reed must not be exaggerated in the first case; in the second, it is indispensable to bring the reed tight against the table so that the stoppage of the tube be complete.

[2] It follows from this fact that for instruments provided with side holes the lowering of intonation due to the influence of a partial closing of the tube or of the application of a reed, is greater on the holes near the apparatus used to produce the vibratory motion than on those farther away. The action of the lips is compared generally with that of the reed. This comparison is not correct. It has been seen that the air-column of tube *E*, set in motion by the breath (§ 23, *b*), gives exactly the same sound F as does this same air-column when it is set in vibratory motion by means of the lips placed against the open end (§ 25).

[3] Since the above was printed, M. Mahillon has come into possession of a sort of Siamese *chalumean*, composed of a long cylindrical tube pierced with several lateral holes. Its air-column is set in vibration by means of a metallic reed glued over a rectangular opening at the other end of the tube, which gives to the whole the appearance of a traverse flute. In spite of the metallic reed, this *chalumean* produces sounds which are higher as the tube is shortened by opening the holes on the side. Hence it follows that when the metallic reed is sufficiently thin it may be substituted in certain cases for the cane reed, of which it acquires the flexibility and properties.

of its own causes the tube to which it is applied to act merely as a reverberator or intensifier while following however the laws of the resonance of tubes. It also explains the fact that the intonation which follows from the association of the reed with the tube, instead of falling with increase of diameter, as is the case with tubes in which the air is set in motion without any intermediary, or at the least by the intervention of the breath or the mouthpiece, follows a contrary law ; it falls with diminution of the diameter. Thus, it has been noticed that a cylindrical tube 414 mm. (16 ⅓ inches) long and 6 mm. (¼ inch) in diameter gives, with an *arghoul*[1] reed, a sound at the

in diameter set in vibration with the same reed gives a sound a minor fifth higher.

pitch of , while a tube of the same length and 12 mm.

[1] The *arghoul* is a very ancient Egyptian instrument (See *Catalogue du Musée*, Nos. 113, 114) and very certainly the primordial type of the association of the vibrating reed with the cylindrical tube.

ON THE FREEZING-POINTS OF AQUEOUS SOLUTIONS OF NON-ELECTROLYTES. II.

BY E. H. LOOMIS.

IN a former paper on the same subject[1] it has been shown that the freezing-points of equimolecular solutions of a large number of non-electrolytes in extreme dilution are the same. Thus it was found that the solutions whose strength is $\frac{1}{100}$ gram-molecule per liter of the solution all freeze at $-0°.0186$ C. This means that the van't Hoff constant is valid for all such solutions and that its value is 1.86. There were three noticeable exceptions, methyl alcohol, ethyl alcohol, and ether, which gave the respective values, 1.82, 1.84 and 1.50. With the desire to make the examination of the problem as complete as possible and with the hope that additional experimental data would perhaps enable us to account for the very important exceptions which these three substances exhibited the work was extended. The results form the material of the present paper.

It is helpful at the outset to examine in some detail the behavior of the thermometer. This thermometer has now been in use for seven years. Its zero-point continues to rise. When it left the Reichsanstalt where it was corrected, its zero was $+0.015$. It is now $+0.057$. During the last period of observation (January–March, 1900) it has risen $0.°0018$ C., as appears by an examination of the successive zero-points which were observed in this period and which are presented in the following table.

These zero-points are each the average of three or four separate determinations which were made in close succession in the early part of the day on which the freezing-points of the solutions were observed.

The old questions suggest themselves:

1. How well do these separate determinations agree among themselves?

[1] PHYSICAL REVIEW, 1899, IX., No. 5, p. 257.

TABLE I.

1 Date.	2 Observed Zero.	3 Barom-eter.	4 Room-Tempera-ture.	5 Zero Cor't to 0°C. and 760 mm	6 Maximum Variation.	7 Depressions Observed on the Given Zero.
1900	°		°			
Jan. 27	+0.0555	763.3	2.0	0.0542	4 in 4 obs.	Salicine.
" 29	0.0545	750.6	2.0	0.0553	1 in 3	Urea.
" 30	0.0556	755.9	2.0	0.0537	2 in 3	Milk-sugar.
" 31	0.0552	748.3	3.0	0.0570	4 in 3	Phenol.
Feb. 1	0.0558	754.4	2.0	0.0559	4 in 3	Levulose and dulcite.
" 2	0.0562	759.7	2.0	0.0555	2 in 3	Acetamid and resorcin.
" 6	0.0593	773.7	2.0	0.0562	1 in 3	Maltose.
" 19	0.0562	755.9	2.0	0.0555	5 in 3	Hydroquinone.
" 20	0.0578	766.1	2.0	0.0560	3 in 3	Pyrocatechin.
" 26	0.0566	756.7	2.0	0.0564	7 in 3	Pyrogallol.
Mar. 12	0.0573	760.5	2.0	0.0564	5 in 3	Benzamid.
" 16	0.0556	744.7	2.0	0.0573	3 in 3	Various controls.

2. How constant does the zero-point of the thermometer remain during a long period of use?

The first question may be answered by reference to the facts given in column 6 of the table, where the difference between the highest and lowest values of the observed zero-point is given for each day of observations. Thus on January 27th, the observed zero was + 0°.0555, and in column 6 it is indicated that this zero was the aver-

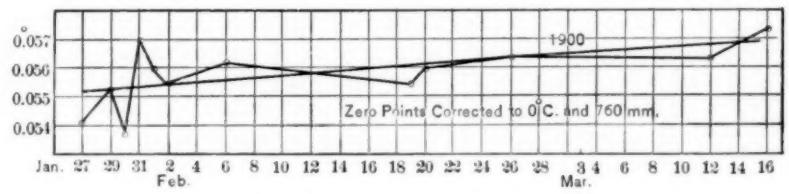


Fig. 1.

age value of four separate determinations which differed among themselves by 0°.0004 C. The greatest variation appeared in the zero-point which was observed February 26th, where it reached the amount 0°.0007 C. in three determinations; while the least variation appeared in the zero-points for January 29th and February 6th when it is only 0°.0001 C. in three determinations. The same satisfactory agreement between the individual observations which make

up a series whose average value is taken as the desired zero point appears also when we examine the observations on the freezing-points of the various solutions. Without going into details a fair idea of the actual fact may be obtained from the following general statement.

For all the solutions of the strength $\frac{1}{100}$ gram-molecule per liter, the average variation is 0°.0002 C. in three observations. In one instance it was as much as 0°.0006 C. (maltose, February 27th), while on the other hand there was no variation at all in three series, namely, those for milk sugar, levulose and acetamid. Of the more concentrated solutions, let us take those whose strength is $\frac{1}{10}$ gram-molecule. In the observations on their freezing-points, the average variation was 0°.0003 C. The least constant series (hydroquinone, February 19th), showed a variation of 0°.0010 C. in two observations, while again three entire series showed no variation whatever.

The second question,—how nearly constant does the zero-point of the thermometer remain during a long period of use may be answered by reference to the facts in column (5), or by an examination of the diagram immediately under the table. The twelve zero-points here recorded show an apparent variation of 0°.0036 C., the most of which comes out in the first three of the series. Here, as in the former series, there is the same unmistakable *rise* of the zero-point. Assuming that the actual rate at which this elevation of the zero-point went on was uniform throughout the period, we find that the total rise was 0°.0018 C. The dotted line in the diagram represents this uniform rise of the zero-point. It must be remarked that the present series of zero-points is not so satisfactory as those of the two previous years. While the total variation which the series exhibits is by no means great, the fact that it is not distributed over the entire series but is crowded into the first three days of observations is very hard to explain. It does not, for example, seem possible for us to explain this very sudden change in the observed zero-point which appeared between January 30th and January 31st, by simply assuming that the observations were here attended by very unusual experimental errors. Such an assumption would require us to believe that the observed zero-point on January 30th was 0°.0015 C. too low and on the following day as much too

high. If this were so, then it would follow almost certainly that the solutions whose depressions were measured in these days would exhibit abnormal results. Thus the depressions for milk sugar, measured on January 30th would have been abnormally small; while those of phenol measured on the following day would have been abnormally great. However, an examination of the results for these two substances furnishes us with no evidence that such was the case.

Does the thermometer then really change its zero-point suddenly? There seems to be no escape from this disagreeable conclusion. Still, such sudden changes are at the worst very rare, and have little influence on the general character of the results. On only one occasion have I detected such a sudden change by direct observation. On February 26, 1898, a series of observations on the zero-point of the thermometer, begun in the morning, was interrupted and finished in the afternoon. The three individual observations of the morning agreed within 0°.0005 C., and gave the average value for the zero-point, + 0°.0538. The first observation in the afternoon series gave + *0°.0521*. I was so amazed at the result that I at once assumed that some impurity had fallen into the water, presumably a bit of salt, and accordingly replaced the water with a fresh portion before going on with the series. The two following observations, however, were + 0°.0520 and + 0°.0519 respectively, thus agreeing with the one already made. Was it possible that the zero-point had fallen 0°.0020 C.? I tried to avoid this conclusion by trying to believe that the scale of the thermometer had been displaced by the jarring. (The thermometer is of the enclosed type with graduations on milk glass.) I found, however, that no amount of jarring resulted in any measurable displacement of the scale. For the present therefore it seems necessary to admit that the zero-point of the thermometer may suddenly change. Before finally accepting this disagreeable conclusion I propose to test the matter by a series of experiments made especially for the purpose. I may be permitted to say here that a full knowledge of all the facts which have come to light during the long period that the author has been occupied with the present method and which he has aimed to submit to the public with as little bias as possible, has always deterred him

from making any claims in regard to the accuracy of the method, much more from fixing any numerical value to the probable experimental error. I may say, however, that this error is certainly not as low as some experimenters have claimed for their methods. In some cases this assumed error has been fixed as low as 0°.0001 C. Suffice it to say that when this limit of error has been actually attained, we may reasonably expect an experimental answer to a number of important questions which as yet are wholly beyond our reach.

The present series of observations includes the compounds in the following table :

TABLE II.

1 Compound.	2 Formula.	3 Grams per Liter of Solution.	4 Gram-Mol. per Liter. (m)	5 Sp. gr. $(\frac{18°}{4°})$ of Solution in (4)	6 Source of Material.
Milk sugar.	$C_{12}H_{22}O_{11}$	68.44	0.20	1.0256	Merck & Co.
Maltose.	$C_{12}H_{22}O_{11}$	68.44	0.20	1.0250	Kahlbaum.
Levulose.	$C_6H_{12}O_6$	36.02	0.20	1.0127	Kahlbaum.
Dulcite.	$C_6H_8(OH)_6$	18.21	0.10	1.0047	Kahlbaum.
Acetamid.	$C_2H_3ONH_2$	11.82	0.20	0.9995	Kahlbaum.
Salicine.	$C_{13}H_{18}O_7$	22.89	0.08	1.0054	Merck & Co.

Together with other usual data the table also gives the specific gravity $\left(\frac{18°}{4°}\right)$ of the various solutions whose strength is 0.10 and 0.20 gram-molecules per liter respectively. The specific gravities were made with a Mohr balance, and are only accurate to within $\pm$ 0.0002.

The detailed observations of the freezing points of the various solution will now be submitted.

MILK SUGAR. JAN. 30, 1900.

The original product was from Merck & Co. After twice recrystallizing it was powdered and exposed to $CaCl_2$ for many days at room temperature. When so treated its composition is $C_{12}H_{22}O_{11}$, H_2O. The solution $m = 0.20$ was made by direct weighing. In the table of results m denotes the number of gram-molecules of the dissolved substance per liter of the *solution* and $\triangle$ the depression of

the freezing-point. Thus $\frac{\Delta}{m}$ denotes the *molecular depression* of the freezing-point. P denotes the number of grams of the substance which a given solution contains per 1,000 grams of water, which is easily calculable when the specific gravity of the given solution is known. This is nearly enough known for any of the dilute solutions when we know the specific gravity of the most concentrated solutions and assume that for the more dilute solutions the specific gravity decreases linearly with the decrease of concentration. By dividing P by the molecular weight of the compound we get the value of m' which is the number of gram-molecules of the substance per 1,000 grams of water. The formula $\frac{\Delta}{m'}$ is then what I shall call the *corrected value of the molecular depression.*

Milk Sugar.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0.0186	1.86	3.432	0.01	1.86
0.02	0.0372	1.86	6.878	0.0201	1.85
0.05	0.0945	1.89	17.313	0.0506	1.87
0.10	0.1907	1.907	34.994	0.1023	1.864
0.20	0.3919	1.959	71.503	0.2089	1.876

It appears that the molecular depression $\frac{\Delta}{m}$ increases with the increase in the strength of the solution, and by assuming experimental errors of $-0°.0002$ for the observed depression at $m = 0.02$

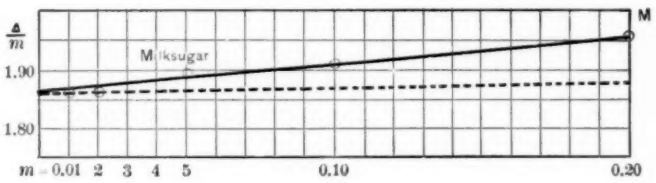


Fig. 2.

and $m = 0.10$, and an error of $+0°.0003$ for the solution $m = 0.05$, this increase in the value of the molecular depression may be said to be *uniform*, as is indicated by the straight line in the diagram.

By extrapolation beyond $m = 0.01$, the value of the molecular depression in extreme dilution is found to be 1.86. It rises to 1.96 at $m = 0.20$. It is to be observed that the corrected values for the molecular depressions, as given by $\frac{\Delta}{m'}$, show the very slight uniform increase from 1.86 to 1.88. These values are represented by the dotted line.

MALTOSE, FEB. 6, 1900.

The original product from Kahlbaum was twice recrystallized from 80 per cent. ethyl alcohol according to the practice of Soxhlet.[1]

The resulting product was perfectly white and yielded a colorless solution in water. According to Soxhlet the maltose so prepared

Maltose.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0.0193	1.93	3.431	0.01	1.93
0.02	0.0378	1.89	6.879	0.0201	1.88
0.03	0.0560	1.87	10.350	0.0302	1.85
0.05	0.0946	1.89	17.316	0.0506	1.87
0.10	0.1919	1.919	35.004	0.1023	1.876
0.20	0.3946	1 973	71.548	0.2091	1.887

should be made up of large, well-formed crystals. A dozen or more attempts to obtain such crystals, however, resulted in failure. In each attempt the crystals obtained were too small to be seen with the unaided eye. The product resembled pieces of ordinary cooking starch. Under the microscope, however, the beautiful crystalline character of the maltose could be seen. The maltose was dried at room-temperature over H_2SO_4 to constant weight. When maltose is so handled its constitution is given by the formula $C_{12}H_{22}O_{11}$, H_2O. The solution $m = 0.20$ was made up by direct weight.

Again it appears that the molecular depression increases uniformly with the increase in the strength of solution. This conclusion requires the admission, however, of considerable experimental errors, + 0°.0006 C. at $m = 0.01$, + 0°.0003 at $m = 0.02$ and − 0°.0005

[1] Soxhlet, Jour. Prak. Chem., 1880, XXI., p. 274.

at $m = 0.05$. The straight line in the diagram represents this uniform rise in the values of the molecular depression. It must be remarked that in this case a curved line with a rather abrupt minimum at

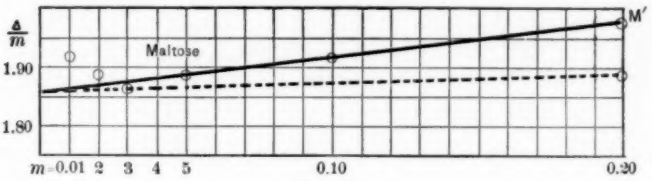


Fig. 3.

$m = 0.05$ would better represent the results. This matter will receive attention in the general discussion of the results.

Here, as in the case of milk sugar, the value of the molecular depression in extreme dilution is 1.86 increasing to 1.97 at $m = 0.20$. The values of the molecular depression obtained by the formula $\frac{\Delta}{m'}$ shows a slight uniform rise from 1.86 to 1.89 as is shown in the diagram by the dotted line.

LEVULOSE. FEB. 1, 1900.

The levulose was from Kahlbaum and bore his label, "Lävulose aus Inulin." It was a mass of large and beautifully formed crystals, which were transparent and exhibited the smallest trace of straw-color. These crystals were permanent in the air, they showed no trace of being hygroscopic and gave a perfectly colorless solution in water. I wish here to express my personal indebtedness to Mr. Kahlbaum for his fidelity to the cause of pure science in the production of such difficult and little used preparations, many of which have been of incalculable value to me in my work. The product was powdered and dried over H_2SO_4. The solution, $m = 1$, was made by direct weight, assuming the formula for levulose crystals, $C_6H_{12}O_6$.

Levulose.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0.0186	1.86	1.804	0.01	1.86
0.02	0.0375	1.88	3.613	0.0201	1.87
0.05	0.0939	1.88	9.062	0.0503	1.87
0.10	0.1890	1.890	18.235	0.1013	1.867
0.20	0.3836	1.918	36.918	0.2050	1.871

Here again the results show a uniform increase in the molecular depression, beginning with the value 1.86 in extreme dilution and

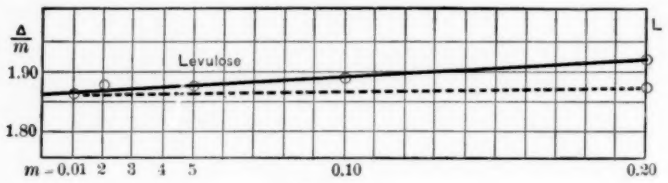


Fig. 4.

rising to the value 1.92 at $m = 0.20$. The formula $\frac{\Delta}{m'}$, shows the very slight increase from 1.86 to 1.87. It is noticeable that these conclusions require the assumption of no appreciable experimental errors in any of the observations.

DULCITE. FEB. 1, 1900.

The original product was from Kahlbaum. It was white and well crystallized. Exposure over H_2SO_4 resulted in no sensible loss of weight. The solution $m = 0.10$ was made by direct weight. The limits of solubility do not permit the solution $m = 0.20$.

Dulcite.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0.0185	1.85	1.825	0.01	1.85
0.02	0.0377	1.88	3.654	0.0201	1.88
0.05	0.0927	1.86	8.969	0.0504	1.84
0.10	0.1877	1.877	18.460	0.1014	1.852

The results show a molecular depression of 1.85 in extreme dilution and a uniform rise to 1.88 at $m = 1.10$. This conclusion is

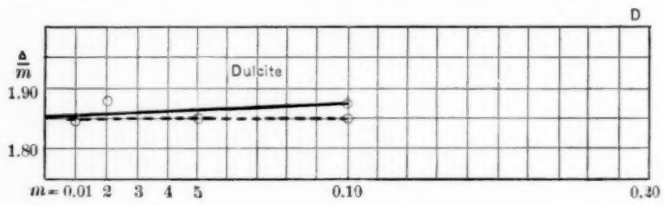


Fig. 5.

represented by the straight line in the diagram and requires the admission of experimental errors of $-0°.0001$ C., $+0°.0004$ C., and

— 0°.0003 C. in the observations, $m = 0.01$, $m = 0.02$ and $m = 0.05$ respectively. The molecular depression calculated with the formula $\frac{\Delta}{m'}$ gives the constant value 1.85 for all concentrations.

ACETAMID. FEB. 2, 1900.

The original product from Kahlbaum was redistilled. The distillate was allowed to crystallize slowly from fusion. After about one-half of the fused product had thus crystallized the remaining liquid was poured off and the crystalline residue dried over H_2SO_4 for some months. It needs to be said that the product still retains a slight odor. The solution $m = 1.0$ was made by direct weight, due attention being given to the fact that acetamid is hygroscopic. The specific gravity of the solution $m = 1$ is 1.0027 at 18° C.

Acetamid.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0.0183	1.83	0.591	0.01	1.83
0.02	0.0362	1.81	1.183	0.02	1.81
0.05	0.0917	1.83	2.962	0.0502	1.82
0.10	0.1835	1.84	5.948	0.1007	1.83
0.20	0.3684	1.84	11.968	0.2026	1.82
1.00	1.878	1.88	61.29	1.0375	1.81

It appears again that the molecular depression increases uniformly with the increase of the solution's strength throughout the entire region from $m = 0.01$ to $m = 1$, providing we assume experimental

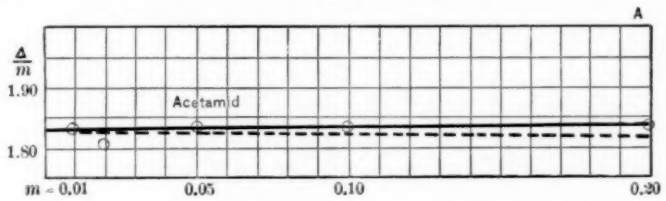


Fig. 6.

errors of — 0°.0004, + 0°.0002 and + 0°.0004 in the observations at $m = 0.02$, 0.05 and $m = 0.20$ respectively. The molecular depression, however, in extreme dilution is *only 1.83*. It rises uniformly to 1.88 at $m = 1.0$. The use of the formula $\frac{\Delta}{m'}$ gives value

for the molecular depression which decrease uniformly from 1.83 to 1.81.

It needs to be remarked that the exceptional character of the molecular depression for this substance came to light in the work done upon it in the year 1899. The fear, however, that this might be due to some impurity in the acetamid or to lack of proper attention to the hygroscopic nature of the substance deterred me from publishing the results until the entire series could be repeated. The two series are identical within the limits of experimental error, and establish the exceptional character of acetamid.

SALICINE. JAN. 27, 1900.

The original product from Merck and Co. was twice recrystalized from dilute ethyl alcohol. It then yielded a colorless solution with water. After long exposure over H_2SO_4 it was made into the solution $m = 0.08$ by weight.

Salicine.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0.0183	1.83	2.870	0.01	1.83
0.02	0.0374	1.87	5.751	0.0201	1.86
0.05	0.0935	1.87	14.475	0.0506	1.85
0.08	0.1497	1.87	23.300	0.0814	1.84

Again the molecular depression shows a uniform increase from 1.86 in extreme dilution to 1.87 at $m = 0.08$. This conclusion

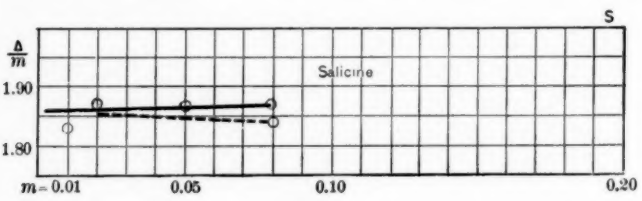


Fig. 7.

requires the admission of experimental errors of $-0°.0002$, and $+0°.0002$ at $m = 0.01$ and $m = 0.02$, respectively. The formula $\frac{\Delta}{m'}$ gives values for the molecular depression which exhibit a uniform decrease from 1.86 to 1.84. I wish to say that I have made

many attempts to obtain new values for the molecular depression of urea, one of the three non-electrolytes examined in 1893. So far the results seem to show that this compound is unstable in aqueous solution. I shall resume work on this compound at the earliest opportunity and shall submit the results as soon as a definite conclusion is reached.

Summary of the Experimental Facts.

The experimental results submitted in this paper confirm the conclusions which were reached on the basis of the work already described in the former paper on the same subject: *Equi-molecular aqueous solutions of non-electrolytes in extreme dilution have the same freezing-points.*

By taking the results of the present paper together with these of the former paper we find that the following compounds in extreme aqueous dilution give 1.86 as the most probable value of their molecular depression:—*n*-propyl alcohol, *n*-butyl alcohol, amyl alcohol, acetone, glycerine, cane sugar, milk sugar, maltose, dextrose, levulose, mannite (1.85), dulcite (1.85), salicine, chloral hydrate and aniline. This indicates that the van't Hoff constant is valid for this large number of substances and that its value is 1.86–1.85.

The exceptions to this conclusion which were found in the former paper were presented by methyl alcohol, ethyl alcohol and ether. The present paper presents an additional exception in the case of acetamide, whose molecular depression, like those for the other exceptional cases, is abnormally low, namely 1.83.

2. Let us now examine the values of the molecular depression as given by the formula, $\frac{\Delta}{m}$, where m denotes the gram-molecules of the compound in 1,000 cc. of the solution.

The experimental results establish the following general statement: *For a given non-electrolyte the molecular depression* $\left(\frac{\Delta}{m}\right)$ *changes uniformly with the concentration of the solution.* Or by using the graphic method of expressing the results we may say that the "curves" which express the molecular depression as functions of the concentrations are straight lines. *The present experimental results do not indicate the slightest maximum or minimum values in*

the molecular depressions within the region of concentration which has been examined. The only exception appears to be ethyl ether. It is necessary, however, to remark that recent experiments made on the evaporation of this compound from its aqueous solutions indicate that the exceptional values of its molecular depression were due to this cause.

It needs further to be remarked that in order to make maltose conform to this general statement of the experimental results, very unusual experimental errors must be assumed. Thus an error of 0°.0006 must be assumed at $m = 0.01$; otherwise a *minimum* value would come to light at $m = 0.03$. I am not satisfied that such an error actually appears in the experimental data, since a repeated observation at $m = 0.01$ gave the same high value. Since this compound is the only one out of eighteen compounds already examined which exhibits the smallest tendency to develop a minimum value of the molecular depression I am unwilling to look upon it as presenting a real exception to our general statement until further work is done upon it.

3. Let us next examine the values of the molecular depressions as calculated from the formula $\frac{\Delta}{m'}$ where m' denotes the strength of the solution in gram-molecules of the solute per *1,000 grams of water*. The quantity m' is easily found for any given value of m when the specific gravity of the solution is known. Obviously m' is greater than m, and the values of the molecular depression $\frac{\Delta}{m'}$ are therefore smaller than the molecular depressions $\frac{\Delta}{m}$. In solutions of extreme dilution where the volume of the solute is negligibly small compared with that of the water in the solution the values of m' and m are practically the same and so also $\frac{\Delta}{m'}$ and $\frac{\Delta}{m}$. As the solution becomes more concentrated the volume of the solute increases and the value of m' diverges more and more widely from that of m. The values of the molecular depression, $\frac{\Delta}{m'}$, may be summarized as follows :

(*a*) *The molecular depressions,* $\frac{\Delta}{m'}$, *remain constant for all the various concentrations of a given solution,* in the cases of methyl alcohol, (1.82–1.81), ethyl alcohol (1.84–1.83), dextrose, levulose (1.86–1.87), mannite, dulcite, glycerine, and chloral hydrate.

(*b*) *In all the other cases the molecular depression* $\frac{\Delta}{m'}$ *changes uniformly with the changes in the concentration of the solution.*

This uniform change is a uniform increase as the strength of the solution increases in the case of the three isomers, cane sugar, milk sugar and maltose.

It is a uniform decrease in the case of *n*-propyl alcohol, *n*-butyl alcohol, amyl alcohol, acetone, acetamide, aniline, and salicine. The change is, however, slight in all these cases except that of aniline where the uniform decrease is from 1.86 in extreme dilution to 1.74 at $m' = 0.20$. This is four-fold greater than that observed in any other compound.

4. It appears further that isomeric compounds have very nearly the same molecular depression not only in extreme dilution but also throughout the whole region of concentration which has been examined. Thus the two isomers dextrose and levulose give nearly the same molecular depression. The pair, mannite and dulcite, have also the same values. The same is the case with the three isomers, cane sugar, maltose and milk sugar. In order to justify this statement rather large experimental errors need to be admitted especially in the case of the three sugars, which have the same value of the molecular depression in extreme dilution but which give the following values at $m' = 0.209$:

Cane sugar,	1.892
Milk sugar,	1.876
Maltose,	1.887

These values correspond to the following freezing-points:

Cane sugar,	$-0°.3784$ C.
Milk sugar,	$-0\ .3952$
Maltose,	$-0\ .3774$

To assert, then, that these three isomers have a common value of the molecular depression carries with it the concession of experimental

errors in the observations on the solutions $m = 0.20$ amounting to as much as 0°.003 C. It needs, however to be noticed that this is still less than one per cent. of the total depression and I think that an error of this magnitude is possible in the more concentrated solutions due jointly to possible errors in the preparation of the original solutions, to errors in the calculation of m' from observation of the specific gravity of the solution and to the errors of the actual observations of the freezing-point itself.

A final decision of this point should be reserved until the freezing-points of these sugar solutions at $m = 0.20$ are redetermined, one after the other in the closest succession. This I shall undertake at the earliest opportunity.

GENERAL DISCUSSION OF THE RESULTS.

Let us now seek to interpret these experimental results with the aid of the conception of osmotic pressure.

1. The fact that equimolecular solutions of a large number of non-electrolytes in extreme dilution have the same freezing-point indicates that the osmotic pressures of such equimolecular solutions are equal. Or, in other words, the osmotic pressure of non-electrolytes in *extreme aqueous dilution* depends solely on the number of molecules of the given compound in a given volume of the solvent and not on the nature of these molecules. This fact in regard to the osmotic pressure is strictly analogous to a fact in regard to the behavior of bodies in the form of a perfect gas, and known as Avogadro's hypothesis.

The only exceptions so far observed are found in methyl alcohol, ethyl alcohol and acetamide.

A possible explanation of the exceptional character of these compounds was one object of the present work and such an explanation is suggested on page 238.

In order to perfectly interpret the facts presented in the summary of the experimental results in paragraph 2 on page 231, namely that the values of the molecular depression $\frac{\Delta}{m'}$ for a given non-electrolyte either remain practically constant or else change uniformly with the concentration we need to call to mind the theoretical

relation which the van't Hoff theory of solution presents between the osmotic pressure and the depression of freezing-point.

By direct application of the second law of thermodynamics to the process by which ice is separated from a solution in course of freezing, van't Hoff has shown that

$$\Delta = \frac{n}{N} \cdot \frac{Tpv}{L} \qquad (1)$$

where the letters have the following significance :

Δ = depression of freezing-point,
n = number of gram-molecules of solute,
N = number of gram-molecules of solvent,
u = specific volume of solute, or the volume of the solution which contains 1 gram-molecule of solute,
T = freezing-point of solvent in absolute temperature,
L = heat-equivalent of fusion of 1 gram-molecule of the solvent, and
p = osmotic pressure.

Now if the osmotic pressure obeys the laws of Boyle and Gay Lussac, we should have pv equal to RT, and could write the van't Hoff equation in the form,

$$\Delta = \frac{n}{N} \frac{RT^2}{L}, \quad \text{or} \quad \frac{\Delta}{n} = \frac{RT^2}{NL}. \qquad (2)$$

On the left of this equation we have the quotient of the depression of the freezing-point (Δ), divided by the concentration of the solution expressed in gram-molecules (n) of the solute per (N) gram-molecules of the solvent.

This is the molecular depression. On the right we have constant quantities alone, if we make our solution so as always to contain the same amount of solvent.

The equation then asserts the fact that the molecular depression of equimolecular solutions of undissociated compounds in a given solvent is the same for all such compounds, and further remains constant for all the various concentrations of a given compound.

To test the validity of this conclusion by comparing it with the present experimental results, let us suppose our solutions to be so prepared as to contain 1,000 grams of water. Then the van't Hoff equation becomes,

$$\frac{\Delta}{n} = \frac{RT^2}{\frac{1000}{18} \cdot L},$$

or by remembering that $\frac{L}{18}$ is the heat-equivalent of melting 1 gram of ice and denoting this by λ we may write,

$$\frac{\Delta}{n} = \frac{RT^2}{1000 \cdot \lambda}. \qquad (3)$$

The concentration (n) of the solution is now expressed in gram-molecules of the solute to *1,000 grams* of the solvent, and the molecular depression is the *constant*, $\frac{RT^2}{1000 \cdot \lambda}$, the numerical value of which is fixed when we know the values of R, T and λ.

T is of course equal to 273, and R may be taken as 1.98 (gram-calories). The value of λ is generally taken as 79 (gram-calories). If, however, we assume λ equal to 79.3 instead, the value of the molecular depression $\frac{\Delta}{n}$ as given in the van't Hoff equation is 1.86.

Now $\frac{\Delta}{n}$ as here defined is what we have uniformly expressed throughout the experimental work by $\frac{\Delta}{m'}$. This value of the molecular depression is actually found to be 1.86–1.85 for all the non-electrolytes in extreme dilution except three, and is found to remain constant for all the various concentrations of the non-electrolytes, levulose, dextrose, mannite, dulcite, glycerine and chloral hydrate. *These non-electrolytes, then, confirm the van't Hoff assumption that the osmotic pressure obeys the gas laws of Boyle and Gay Lussac.*

The other non-electrolytes are found not to conform to these simple gas laws. Thus the three sugars, cane sugar, milk sugar and maltose exhibit an increase in the value of $\frac{\Delta}{m'}$, with increase in the concentration. From equation (1) then we should conclude that this may be due to the fact that the product (pv) increases with increase of concentration, or these bodies in aqueous solution do not

obey Boyle's simple law. The small departure from this law may be perhaps accounted for by use of the same considerations which lead to the application of van der Waals' correction to the volume of a gas when much compressed. The admissibility of such a correction is the more evident if we bear in mind the fact that in the case of these sugars we are dealing with very massive molecules and most likely with unusually large ones as well.

The remaining non-electrolytes all show a uniform decrease of the molecular depression $\frac{\Delta}{m'}$, as the concentration increases. This indicates that the product (pv) of osmotic pressure p and volume v decreases with the concentration. In no case, however, is this decrease more considerable than the decrease in the analogous product in the case of some actual gases, and the departure from the simple law in the present cases may be accounted for by making the obvious assumption that here as in the case of gases an increase in the concentration of the molecules brings about a condition in which the attractions between them begin to play a rôle, the importance of which becomes greater as the solution becomes more and more concentrated. In the case of aniline, however, such an assumption is obviously inadequate to explain the very rapid decrease in the molecular depression, amounting to not less than 7 per cent. between the molecular depression in extreme dilution and that at $m = 0.20$.

The decrease is here so marked that the thought at once suggests itself that it may be due to an "association" of the molecules of this particular non-electrolyte which would decrease the osmotic pressure and so cause a decrease in the value of $\frac{\Delta}{m'}$.

The need of making such an assumption of "molecular association" had not presented itself at any point in the great mass of work already done on the non-electrolytes, and I was unwilling to adopt it in this particular instance until additional experimental material was at hand. For this purpose I entered upon an examination of all available chemical compounds of a constitution similar to that of aniline. There are, of course, only a few such compounds that can be had pure and at the same time sufficiently soluble in

water for the present purpose. These are phenol, pyrocatechin, resorcinol, hydroquinone, pyrogallol and benzamide.

Reserving the experimental data for a subsequent paper it may be stated here that each one of these compounds behaves exactly the same as aniline—*the molecular depression decreases at a rapid rate with increase of concentration.* The assumption, then, that the molecules of each of these closely related non-electrolytes combine to form molecular aggregates the number and complexity of which increase with the increase of the concentration is one that easily explains the behavior of this important group of aqueous solutions. We are warranted, I think, in believing that the present facts point to a general law, namely: *The benzene derivatives in aqueous solution exist in the form of molecular aggregates, the number and complexity of which increase with increase in the concentration of the solution.*

The final acceptance of this conclusion can come only after the fullest experimental examination of the matter; and to this end it is important to determine by experiment whether the molecular elevation of the boiling-points and the vapor densities of this group of compounds indicates the same tendency of these compounds to former molecular aggregates. If this should turn out to be the fact there would remain little doubt in regard to the validity of the assumption which is here made in regard to the "association" of these molecules.

In this place attention may be given to the facts presented by the three non-electrolytes, methyl- and ethyl-alcohol, and acetamide. These three compounds exhibit an abnormally low value of the molecular depression throughout the whole range of concentration, and also a slight decrease in the value as the concentration increases.

This latter fact may be easily enough accounted for by the hypothesis that the crowding together of the molecules in the more concentrated solutions brings into play molecular forces which cause the product (pv) to decrease. But how shall we account for the "abnormally" low values which the molecular depressions of these three compounds develop in *extreme dilution.* I am disposed to think that the real explanation lies in the fact which has been brought to light in the case of aniline and its related compounds. Here, as

in these other cases, the formation of molecular aggregates may offer a complete explanation.

The very general fact in regard to the increase of the values of the molecular depression $\left(\frac{\triangle}{m}\right)$ as stated in §2 on p. 231 is a mere consequence of the way in which the solutions were prepared, namely so as to contain m gram-molecules per 1,000 cc. of the solution. It is obvious for a given solution containing a given number of grams of the solute and having an observed depression ($\triangle$), that the value of m is less than that of m', and that the difference becomes more and more marked as the strength of the solution increases. This accounts for the fact that the values of the molecular depression $\frac{\triangle}{m}$ diverge upward from that of $\frac{\triangle}{m'}$ with increase of concentration.

3. The results of the experimental examination of the twenty-six various non-electrolytes presented in the present papers and the former one on the same subject shows that none of these compounds exhibit "abnormally high" values of the molecular depression in the region of extreme dilution. In all cases the molecular depression in extreme dilution is either 1.86–1.85 or else it is less than this amount. We thus have at hand a large mass of evidence which shows that *the non-electrolytes do not suffer the slightest dissociation in extreme dilution.*

PHYSICAL LABORATORY, PRINCETON UNIVERITY.

THE FORMULA FOR THE DEPRESSION OF THE FREEZING TEMPERATURE OF SOLUTIONS.

BY WILLIAM FRANCIS MAGIE.

THE formula first developed by van't Hoff for the depression of the freezing temperature of a solution below that of the solvent, and commonly used in comparing the results of experiment with the theory, is evidently only an approximate one. In view of the increasing accuracy with which this depression has been measured by Loomis, and the general confirmation of van't Hoff's law which his results furnish, it becomes a matter of interest to inquire whether the departures from the law exhibited by some of his results are due to the insufficiency of the formula or are to be ascribed to other causes. To carry out this inquiry we may use the thermodynamic method introduced by van't Hoff, and proceed to a closer approximation by noticing the circumstances:

1. That the cyclic process employed is not a simple or Carnot's cycle; 2. That many of the quantities which enter the formulas are variable with the temperature.

The solution employed is made up by dissolving n gram-molecules of solute in N gram-molecules of solvent, both n and N being very large numbers. This solution is enclosed in a vessel furnished with a semi-permeable membrane and the following cyclic process is executed with it:

1. The solution being at the absolute temperature t, the freezing temperature of the solvent, a mass of the solvent w is expressed through the membrane. Work will be done by the pressure p required to force out the solvent. On the condition that the quantity of the solution is very great, the pressure will remain constant during this operation and the work done by it in reducing the volume of the solution by the volume v may be represented by pv to any required degree of approximation. At the same time heat will be

developed in the solution, which must be abstracted from the solution to keep its temperature constant. This may be expressed by μv, if μ represents the heat which must be removed in this manner when the volume of the solution diminishes by unity at the temperature t. We may call μ the latent heat of expansion.

2. Heat is then removed from the system at the temperature t, until the expressed solvent is solidified. If we represent by λ the latent heat of liquefaction of the solvent at the temperature t, the quantity of heat thus abstracted is $w\lambda$.

3. The temperature of the system is then lowered by the further abstraction of heat until its temperature becomes t'', the freezing temperature of the more concentrated solution. The heat removed may be represented by

$$s''(W - w)\,(t - t'') + \sigma w\,(t - t'')$$

if s'' and σ represent the specific heats of the more concentrated solution and of the solid solvent respectively and W the mass of the original solution.

4. The solid solvent is then immersed in the solution and melted by the introduction of heat. As it melts the solution will become more dilute and the temperature will rise, until when the melting is completed it reaches the temperature t', the freezing temperature of the original solution. The quantities of heat actually introduced to effect this change might be represented by symbols, and introduced explicitly in the final equations; but it is more convenient to proceed in another way. It has been assumed that the quantity of solvent employed is very great, so that the change in concentration caused by the melting of the solid solvent in it, and so also the rise of the freezing temperature, will be very small. We may therefore set $t'' = t'$ and consider the latent heat of liquefaction as constant, to any desired degree of approximation. The heat introduced to melt the solid solvent will then be expressed by $w\lambda'$, where λ' is the latent heat of liquefaction at the temperature t'. The heat introduced to raise the temperature of the solution from t'' to t' will be balanced in the final equations by that abstracted in lowering the temperature of the solid solvent and of the solution from t' to t'' in operation 3 to a degree of approximation which may be made

as close as we please by the use of a very great amount of solution.

5. The solution is then raised to its original temperature t by the introduction of the quantity of heat represented by $s' W(t - t')$, if s' represents the specific heat of the original solution.

The cyclic process is then complete. It is a reversible process and we may accordingly write the equations of energy and entropy for it. Considering $t'' = t'$, these become

$$(a) \quad \mu v + w(\lambda - \lambda') + \{s''(W - w) - s' W + \sigma w\}(t - t') = pv.$$

$$(b) \quad \frac{\mu v}{t} + w\left(\frac{\lambda}{t} - \frac{\lambda'}{t'}\right) + \{s''(W - w) - s' W + \sigma w\} \int_{t'}^{t} \frac{dt}{t} = 0.$$

The integral $\int_{t'}^{t} \frac{dt}{t} = \log \frac{t}{t'}$ which occurs in equation b may be expanded in a series of which it will be sufficient to retain the two terms, $\frac{t - t'}{t'} - \frac{(t - t')^2}{2t'^2}$. Dividing equation a by t', combining the two equations and reducing, we obtain

$$(c) \quad (t - t')\left\{\mu v + w\lambda + [s''(W - w) - s' W + \sigma w]\frac{t - t'}{2} \cdot \frac{t}{t'}\right\} = tpv.$$

This equation is valid for any solution, whatever the solute may be, and however much dissociation or association there may be in the solution. It involves only the assumption that a definite pressure exists by which the solvent may be forced out of the solution through a semi-permeable membrane. The approximations involved in it, except that in which the third and subsequent terms of the expansion of $\log \frac{t}{t'}$ are neglected, depend on the amount of the solution employed, and may be pushed to any degree required by the use of a sufficiently large amount of the solution.

The term in the parenthesis which is of the most importance is $\omega\lambda$. Neglecting the other terms in the first approximation we obtain van't Hoff's formula for the depression of the freezing temperature

$$(d) \quad t - t' = \frac{tpv}{w\lambda}.$$

We may substitute this value of $t - t'$ in the specific heat term

in the parenthesis, setting $\frac{t}{t'} = 1$, and obtain a formula for the depression of the freezing temperature which is correct to a second approximation.

In case the solution is one in which the osmotic pressure is proportional to the absolute temperature I have shown in a previous paper[1] that

$$(e) \qquad \mu = p$$

and that

$$(f) \qquad s''(W - w) - s'W + sw = 0,$$

where s represents the specific heat of the solvent.

In that paper it was shown by experiment that the relation embodied in equation f holds true for many solutions of non-electrolytes in water. For these solutions equation e will also hold true.

The general formula may therefore be modified for the case of non-electrolytic solutions into the form

$$(g) \qquad (t - t')\left\{w\lambda + pv + [\sigma - s]\frac{tpv}{2\lambda}\right\} = tpv.$$

If we set M for the mass of the solvent and n for the number of gram-molecules of solute dissolved in it, and assume that the mass w is the mass of solvent which is associated with one gram-molecule of solute in the solution, we obtain for the molecular depression in terms of a standard M,

$$(h) \qquad \frac{t - t'}{n} = \frac{tpv}{M\lambda + npv + (\sigma - s)\frac{ntpv}{2\lambda}}.$$

The volume v is the volume which contains one gram-molecule of solute in the solution.

This formula holds whether or not the osmotic pressure conforms to Boyle's law but requires a constant ratio between the osmotic pressure and the absolute temperature. If the osmotic pressure conforms to the laws, of gases, we may write $pv = Rt$, where R is the gas-constant, and may calculate the depression and examine the

[1] PHYSICAL REVIEW, Vol. IX., No. 2, August, 1899.

influence of the correction terms of the denominator upon its value. Setting $R = 84490$, in which the gram-weight is the unit of force, λ for water $= 79.3$[1] and $M = 1{,}000$ grams we obtain in the first approximation $\frac{t - t'}{n} = 1.855$. Further, setting $\sigma = 0.5$ calorie and $n = 1$, we find that the effect of the two correction terms, which are nearly equal and of opposite sign, is to reduce this value only by 0.001 or to 1.854; an effect far too small to be detected by the present methods of measurement. These terms will be of similar magnitude relative to the principal term of the denominator in any solution that is fairly dilute. It appears, therefore, that the first approximation gives us a formula which is sufficiently exact for our present needs and that the departures exhibited by many solutions from the law of proportionality between the depression of the freezing temperature and the concentration are to be accounted for on other grounds than the insufficiency of the ordinary formula.

PRINCETON UNIVERSITY.

[1] Loomis, PHYSICAL REVIEW, Vol. IX., No. 5, November–December, 1899.

ON THE ACTION OF THE COHERER.

By K. E. Guthe.

I. The Critical Voltage.

In a former paper[1] Trowbridge and I have shown that a coherer with one contact shows quite a regular behavior, when cohesion is produced by a current flowing through it. Its P. D. during the passage of the current increases with the latter, finally reaching a constant value which is independent of a further increase of the current, or changes in the applied E.M.F. We have called this value the critical voltage of the coherer and have determined the same for a few metals.

It has seemed of interest to extend the investigation to a larger number of metals, and the present paper contains the results with coherers of silver, copper, zink, aluminium, cadmium, tin, iron, German silver, nickel and bismuth.

The coherer had practically the same form as the one described in the former paper. Instead of metal balls I used spherical surfaces stamped out of metal sheet. The coherer had one contact only and its resistance could be adjusted by means of a fine screw.

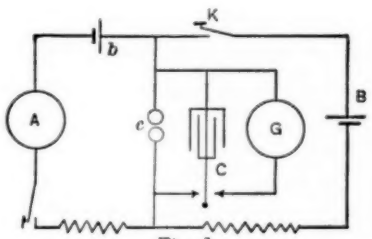


Fig. 1.

The method employed is illustrated by Fig. 1; in which c is the coherer. In order to estimate its original resistance it was connected with an auxiliary circuit containing a low E.M.F. ($b = 0.4$ V.) and a milliammeter (A). After adjustment to a high resistance, cohesion was produced by closing the key K; while the current was flowing, the condenser C was charged and discharged though the galvanometer (G) which had been previously calibrated by means of a stand-

[1] Guthe and Trowbridge, Phys. Rev., XI., p. 22, 1900.

ard cell. Thus the P. D. at the terminals of the coherer could easily be calculated from the deflection of the galvanometer. After opening the key K, the auxiliary circuit was closed again, to ascertain if a lowering of resistance had taken place. Since it was desired to determine the critical voltage only, no accurate measurements of the current were made, though I assured myself in every case by varying the current, that the critical voltage had been reached.

(a) Contact Between Surfaces of the Same Metal.

For each metal I took a series of 30 to 40 observations. The deflections due to the discharge of the condenser varied very little in each series. In the following table the mean values of the deflections (d) and the critical voltages (V) are given.

TABLE I.

	Ag.	Cu.	Zn.	Al.	Cd.	Sn.	Fe.	Germ. S.	Ni.	Bi.
d	13.7	21.6	22.2	54.3	25.1	21.9	51	32	46.9	42
V	0.062	0.094	0.096	0.236	0.109	0.095	0.222	0.139	0.204	0.183

It will be seen that the critical voltage varies appreciably where different metals are used; for German silver it lies between those of its constituent parts. The critical voltage seems to stand in a certain relation to the atomic weight of the metal. If we multiply the two together, we obtain the following results:—

TABLE II.

Ag.	Cu.	Zn.	Al.	Cd.	Sn.	Fe.	Ni.	Bi.
6.71	5.96	6.18	6.39	12.22	11.22	12.43	11.93	39.06

Ag, Cu, Zn and Al give practically the same product: 6.31; Cd, Sn, Fe, Ni, a value almost twice as large: 11.95, while Bi stands alone with a product six times larger than the smallest: $39.06 = 6 \times 6.51$. In the paper mentioned above we found for Pb, $V = 0.127$ volt which gives, multiplied by the atomic weight of Pb; $26.28 = 4 \times 6.57$. The first four metals are the best conductors of heat or electricity, while Pb and Bi stand alone in this respect also.

Interesting as this distinct division of the metals into three groups is, especially when we consider the great differences in the

atomic weights of metals in the same group, there is not enough material on hand to form any definite hypothesis as to the reason for it.

(*b*) *Contact Between Surfaces of Different Metals.*

In the former paper a close agreement was noted between the formula expressing the P. D. of the coherer as a function of the current and the formula[1] which I have found to represent the polarization of Cu electrodes in $CuSO_4$ solution, and we were led to believe that we had to do with a phenomenon somewhat similar to the electrolytic conduction of electricity. We assumed that the existence of a critical voltage is due to the resistance of a layer of small metallic particles (ions or electrons) carried over by the current.[2] Supposing that these particles travel in the direction of the current, we might expect when working with a coherer, having different metals at the two sides of the contact, to obtain the critical voltage of the one or the other metal according to the direction of the current. That this is not the case is shown by the data in Table III. in which are given the critical voltages for a large number of combinations. The current is supposed to flow from the metal in the horizontal to that in the vertical line. The method of observation was the same as in the preceding experiments.

TABLE III.

From :

To:	Ag.	Cu.	Zn.	Cd.	Sn.	Fe.	Germ. S.	Ni.	Bi.
Ag.	0.0622	0.082	0.125	0.127	0.164	0.156	0.078	0.209	0.13
Cu.	0.086	0.094	0.135	0.142	0.170	0.252			0.13
Zn.	0.119	0.143	0.096	0.109	0.103	0.141			0.117
Cd.	0.118	0.131	0.105	0.109	0.087	0.174	0.091		
Sn.	0.166	0.179	0.089	0.087	0.095	0.210	*c* 0 2	0.152	*c* 0.13
Fe.	0.300	0.278	0.141	0.152	0.152	0.222	0.243	0.300	0.22
Germ. S.	0.078			0.10	*c* 0.20	0.261	0.139	0.170	0.165
Ni.	0.122				0.109	0.287	0.191	0.204	0.117
Bi.	0.26	0.261	0.196		*c* 0.22	0.304	0.209	0.196	0.183

[1] Guthe, PHYS. REV., VII., p. 193, 1898.

[2] It can easily be shown by a measurement of the resistance of the coherer, by means of an alternating current, that we have a *metallic* contact, after cohesion has taken place. Using the well-known Kohlrausch method for measuring electrolytic resistances, the value found agreed well with the one calculated from the P.D. and the current. The telephone could be adjusted to absolute silence which shows conlusively the existence of an actual metallic contact.

The deflections of the galvanometer were in general quite concordant; only with Al as one side of the coherer the results were so unsatisfactory that they have been omitted from the table.

We see that in general the direction of the current has no appreciable influence upon the critical voltage between different metals. Differences of considerable size were observed between Bi and Ni and between Fe and Sn only. The Peltier effect can hardly be adduced as the sole explanation for these differences, since they are in opposite direction for Bi and Ni and do not appear for German silver at all. We shall see under III. that the heating of the point of contact may have an influence upon the critical voltage and may possibly explain the observed differences due to the direction of the current.

II. The Negative Action of the Coherer.

Under "negative action" I understand the increase of resistance which can sometimes be observed in coherers when responding to an electrical influence. All the metals studied by me, especially the soft metals, show this behavior under certain conditions. Bose[1] has recently declared this negative action to be the normal one for certain metals. He supposes that each metal exists in two modifications, one with a high resistance (modification A) and another with a low resistance (modification B). The difference between these two, he thinks, is to be sought in the different arrangement of the molecules in the two cases. In certain metals, which he calls positive, *e. g.*, Fe, the modification A is the normal, in others, *e. g.*, K modification B. Under the influence of an electric wave the surface of the metal is supposed to change from its normal state into the other, and thus strains are produced in the metal. Though further action of the electric waves the new arrangement of the molecules may suddenly break down and the resistance of the coherer return more or less to its original value. Thus "oscillatory changes in the molecular structure are produced, which are evidenced by the corresponding electrical reversals."

Bose used in all his experiments the ordinary form of coherer, having a great number of contacts. Mizuno[2] investigating the in-

[1] Bose, Proc. Roy. Soc., 65, p. 166, 1899 and 66, p. 450, 1900.
[2] Mizuno, Phil. Mag., 50, p. 445, 1900.

fluence of repeated electrical impulses upon the resistance of such coherers, found curves of very similar character to Bose's for positive metals; even potassium showed a large final drop in resistance instead of an increase which should have been expected according to Bose's theory. In one case Mizuno used a one-contact coherer (two lead balls) and here the resistance fell after a few sparks of the oscillator to a constant minimum without showing any reversals at all.

It seems possible to arrive at an explanation of the negative action only from experiments with a coherer of a similar form. The phenomenon as observed by me, was as follows: On the first adjustment of the coherer the needle of the milliammeter showed quite irregular movements before it became steady. On closing the main circuit the resistance increased, but when, by opening key K the auxiliary circuit was closed, I observed an unsteady, slowly increasing deflection of the milliammeter showing that the low resistance was formed again. This corresponds perfectly to Bose's description "of the rumbling noise in the telephone due to the rearrangement of the surface molecules to a more stable condition."

It suggested itself immediately that a small, loose particle formed a conducting bridge between the coherer surfaces, which was thrown aside on the introduction of a higher E.M.F., but fell back to its original position, when only a low E.M.F. was in the circuit. This would be quite similar to the action of Nengschwender's anticoherer. The following observations showed this supposition to be true.

While under normal conditions a slight increase of pressure reduced the resistance almost to zero, it remained always relatively high in spite of an appreciable pressure, when the coherer showed negative action. The conducting particle remained between the surfaces.

The increase of resistance could be brought about many times in succession, if the coherer was left undisturbed. Sometimes the resistance became infinite and remained so. In such a case the surfaces had to be brought nearer together in order to make a new adjustment to a high resistance possible. After this the normal action took place. The particle had been thrown aside.

This shows that the negative action of the coherer is due to disturbing influences and cannot be considered a normal phenomenon, as Bose supposes. We shall not be able to understand the nature of the coherer unless we experiment with coherers of a form as simple as possible. The usual form, it seems, is not at all suited to the purpose.

In a paper, which has just appeared, Marx[1] describes his experiments with the so-called Schaefer anticoherer. The original resistance of this instrument is due to small particles forming a bridge between the two metallic ends. He observed under the microscope a distinct motion of the particles when an electric wave fell upon the apparatus, and a falling back into their original position when the electrical influence ceased.

III. The Influence which the Heating of the Contact has upon the Resistance of the Coherer.

It is well known that, after cohesion has taken place, a slight heating of the coherer restores the original high resistance; but it would be wrong to conclude from this that a coherer is less sensitive at higher temperatures. Considering the smallness of the contact, there can be no doubt that even with small currents a development of heat must take place at that point. With metals of low melting point I had observed the heating effect during the previous experiments. In general I was unable, when examining the contact by means of a microscope, before and after being used, to detect the slightest change on the metallic surfaces. But in the case of Bi and Sn, melting took place when the current was increased to more than one ampère. With the other metals I could not observe any change even with currents as large as four ampères.

In the course of my experiments on this subject I was led to the observation of a phenomenon, which, as I believe, was hitherto unknown. The method was practically the same as above. The coherer was slightly changed by using two fine wires of the same metal and at right angles to each other instead of the spherical surfaces. By a light pressure against one of them the loose contact was effected. Now I sent by means of a separate circuit a current of such

[1] Marx, Phys. Zeitschr., Jan. 26th, 1901.

strength through one of the wires that it—and consequently the point of contact too—became heated. While the heating took place the main circuit was closed and the P .D. of the coherer measured.

The higher the temperature of the contact, the lower appeared the resistance of the coherer under otherwise similar conditions and the resistance returned to its original high value when the heating ceased.

The following tables may serve to illustrate this phenomenon. In the first column I have given the deflections obtained by the discharge of the condenser when cohesion was produced before the contact was heated. In the second column follow the deflections obtained while the heating took place, and columns 3 to 5 give the corresponding deflections 10, 20 and 50 seconds after the heating had ceased. The coherer consisted of steel wires of 0.36 mm. diameter. Unit deflection corresponds to 0.00435 volt.

TABLE IV.

174	3	31	102	160
121	23	56	159	160

Even when the original resistance was infinite (this may be expressed by ∞) the phenomenon could be very distinctly observed.

TABLE V.

∞	18	292	∞	∞
∞	19	229	∞	∞

The results obtained when the current through the wire and consequently the temperature of the contact was varied, are given in Table VI. In the first column the heating current is given, the following columns have the same meaning as before. The values in the second column depend on the accidental original adjustment.

TABLE VI.

0.2 amp.	138	121	122	139	139
0.5 amp.	90	12	95	95	95
4.0 amp.	86	5	11	34	75

Similar results were obtained with copper wires. With them the heating seemed to have a still larger influence than with steel. The deflections were only two or three scale divisions during the heating, even in cases in which the original resistance had been infinite. The lengthening of the wire due to the higher temperature produced slipping and made the observations rather difficult, but this could easily be avoided by holding the wire in its original horizontal position with a fine vertical spiral.

Finally I used a contact between wires of different diameter. If we produce cohesion in such an instrument by sending a relatively large current through both wires, the thinner wire will be heated. The observations showed now a decided influence of the direction of the current. This can hardly be due to the different curvature of the wires, since Trowbridge and I have shown, at least for steel balls, that the diameter has no influence upon the critical voltage.

I select for illustration one example out of a great many. The thickness of the steel wires was 1.65 and 0.27 mm. respectively. When a current of three ampères was sent from the thicker to the thinner wire I obtained by discharging the condenser a deflection of 136 scale-divisions. If the current is smaller, the differences are smaller. The P. D. of the coherer is therefore lower if the electricity flows from the hotter to the colder side than if it flows in the opposite direction.

This may enable us to understand why different critical voltages were obtained according to the direction of the current, when contacts with different metals were used (Table III.). Bi showed the discrepancy most of all. If Bi forms one side of the coherer this side will be much warmer than the other, since this metal is a very bad conductor of heat. This would demand a small P. D. if the current flows from Bi to another metal. On the other hand when a current flows in this direction the point of contact is cooled and we might expect a higher critical voltage. These two influences are doubtless of a secondary nature and must be superposed. With Bi, as Table III. shows, the influence of the difference in temperature is by far the greater, while with Ni the Peltier effect seems to be the stronger.

I believe that in the action of the coherer the heating of the contact plays an important rôle. By it the first impulse to the lower-

ing of resistance is given ; it may be called the first stage. We have to keep in mind that when the contact is not heated by the current passing *through* the coherer, the resistance very soon increases on cooling, while after actual cohesion has taken place, a metallic contact is produced and the resistance returns only very slowly to its high value.

PHYSICAL LABORATORY, UNIVERSITY OF BERLIN, January, 1901.

NEW BOOK.

Livre Jubilaire: Recueil travaux offerts par les auteurs à H. A. LORENTZ, professeur de physique à l'université de Leiden. Le Haye; Martinus Nijhoff, 1900. Pp. ix + 678.

The eleventh of December, 1900, was the twenty-fifth anniversary of the conferring of the doctor's degree upon the eminent physicist, H. A. Lorentz; and the occasion was celebrated by the presentation to him on behalf of his colleagues of a very notable collection of memoirs gathered together in a jubilee volume. The committee consisting of Professors Booscha, Haga, V. A. Julius, W. H. Julius, Onnes, Siertsema, Sissingh, VanderWaals, Wind and Zeeman are to be congratulated upon the brilliant success of their work. The collection is the more remarkable when we consider the short time allowed to the various authors for the completion of their work. It consists of 58 papers which make a book of nearly seven hundred pages. These were published as a separate volume of the Archives of the Society of Sciences at Harlem.

Of the purely theoretical papers which constitute the most important part of the collection, eighteen deal more or less directly with problems arising from the consideration of the mechanics of the ion, the foundation of the theory of which is largely due to Lorentz. To this group belong the contributions of V. A. Julius, Farkas, Wien, Kaufmann, Planck, Riecke, Poincaré, Righi, Voigt, Sagnac, Cohn, Garbasso, Wiechert, Wind, J. J. Thomson and des Coudres. Boltzmann in a brief note and Berthlelot at considerable length discuss the equation for the pressure of gases and in particular the expression of the same deduced by Lorentz.

There could scarcely be imagined a more gratifying tribute to the genius of that physicist nor better illustration of the deep impression made upon the mathematical physicists of our day by the views propounded by him in the famous memoir entitled, *Versuch einer Theorie der Elektrischen und optischen Erscheinungen in bewegten Körper* (Leiden, 1895). The development of the theory at the hands of the writers just named leads to a number of startling conclusions. We are told that gravitational disturbances are transmitted with velocity equal to that of light; that gravitation itself is modified by the motion of the attracting bodies; that mass as defined in terms of inertia is constant only for small velocities and increases with the velocity of the moving body; that the first and second of Newton's Laws of motion are to be regarded as rigorous only when we take into account the effects of motion in the surrounding ether; that the principle of equality of action and reaction is not rigorously applicable when applied to matter alone. The modifications which the establishment of these new views would compel us to intro-

duce into the older mechanics become appreciable only when we have to deal with very high velocities. It is chiefly by the careful study of planetary motion or possibly in the domain of the kathode rays that we may, if at all, look for experimental verification of the theory. Poincaré at the close of his paper cites a computation by Lienard to the effect that the complementary force necessary to balance the recoil of a machine of 100 kilowatts would be only $\frac{1}{600}$ of a dyne.

That the Lorentz Jubilee volume, in addition to these papers which deal more or less directly with theoretical issues raised by him, contains much other interesting material will be seen from the following table of contents:

Bernard Brunhes, Sur la réflexion interne dans un cristal doué du pouvoir rotatoire; V. A. Julius, Sur l'action subie par un conducteur chargé dans un champ d'intensité constante; Lord Rayleigh, On the stresses in solid bodies due to unequal heating, and on the double refraction resulting therefrom; H. Pellat, Réflexions au sujet de l'univers et des lois naturelles; Wilder D. Bancroft, Reaction velocity and solubility; Edm. van Aubel, Sur les résistances électriques des métaux purs; Julius Farkas, Allgemeine Principien für die Mechanik des Aethers; Ludwig Boltzmann, Notiz über die Formel für den Druck der Gase; E. Mathias, Sur la loi de distribution de la composante horizontale du magnétisme terrestre en France; W. Wien, Ueber die Möglichkeit einer elektromagnetischen Begründung der Mechanik; G. Tammann, Ueber die Lage der Volumen- und Energiefläche eines Krystalls und seiner Schmelze; N. Schiller, Einige thermodynamisch abzuleitenden Beziehungen zwischen den Grössen, die den physikalischen Zustand einer Lösung characterisiren; W. Kaufmann, Ueber die Schwingungsamplitude der Electronen; A. Turpain, Etude expérimentale sur le résonnateur de Hertz; Max Planck, Ueber die von einem elliptisch schwingenden Ion emittirte und absorbirte Energie; G. Guglielmo, description d'une simple balance magnétique; Eduard Riecke, Ueber characteristische Curven bei der electrischen Entladung durch verdünnte Gase; G. J. W. Bremer, Indices de réfraction de solutions de chlorure de calcium; F. A. H. Schreinemakers, La tension de vapeur de mélanges ternaires; P. Duhem, Sur la théorie électrodynamique de Helmholtz et la théorie électromagnétique de la lumière; P. Zeeman, Weiteres zur unsymmetrischen Aenderung der Spectrallinien in einem Magnetfelde; H. du Bois, Toupie magnétocinétique; illustrant les phénomènes para- et diamagnétiques; H. Poincairé, La théorie de Lorentz et le principe de la réaction; G. H. Bryan, Energy accelerations. A study in energy partition and irreversibility; Ernest Cohen, Ueber die Bestimmung der Arbeit, welche die Verwantschaft leisten kann; J. P. Kuenen, Mixtures of hydrochloric acid and methylen ether; G. Bakker, Théorie de l'induction

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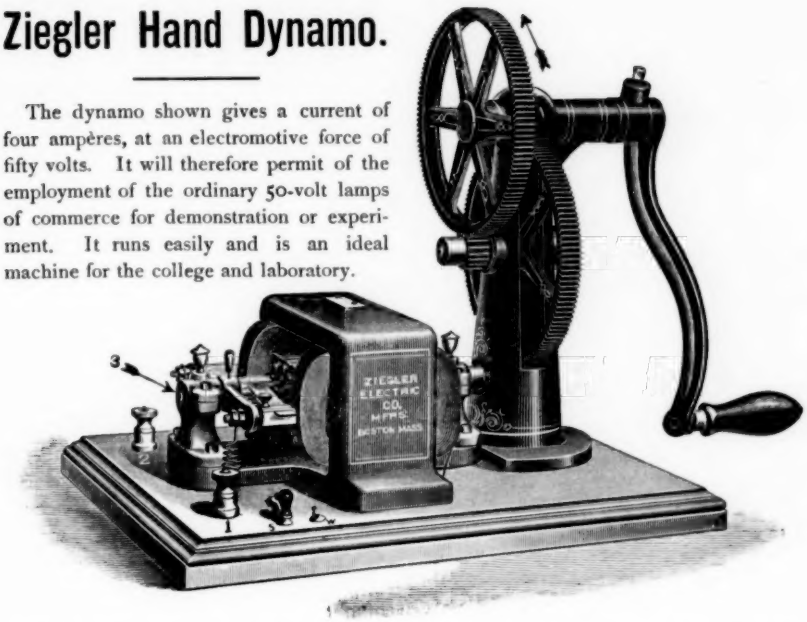

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